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De subjecto vetustissimo
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GALILEO GALILEI.

Gjorn III, nuove scienze.

THE ELEMENTS OF

ATOM-MECHANICS.

BY

GUSTAVUS DETLEF HINRICHS, M. D., LL. D.

VOLUME FIRST.

THE

TRUE ATOMIC WEIGHTS

OF THE CHEMICAL ELEMENTS AND THE

UNITY OF MATTER.

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TRUE ATOMIC WEIGHTS

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—BY—

GUSTAVUS DETLEF HINRICHS, M. D., LL. D.,

HONORARY AND CORRESPONDING MEMBER OF SCIENTIFIC SOCIETIES IN FRANCE, GERMANY AND THE UNITED STATES; PROFESSOR OF CHEMISTRY, ST. LOUIS COLLEGE OF PHARMACY.

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TO

MARCELIN BERTHELOT,

PROFESSOR OF THE COLLÈGE DE FRANCE,
MEMBER OF THE INSTITUTE.

THIS VOLUME

IS DEDICATED BY,

THE AUTHOR.

MONSIEUR M. BERTHELOT,
SÉNATEUR,
Secrétaire perpétuel de l'Académie des Sciences,
PARIS, FRANCE.

MY DEAR SIR:

Kindly permit me to dedicate this first volume of my Elements of Atom-Mechanics to your honored name.

More than twenty years ago you presented to the Academy, for insertion in the Comptes Rendus, a number of my contributions to this new science.

When, after my exodus from Darkest America, I was able to resume the publication of my results, you had reached the highest position attainable in science; nevertheless, you again kindly accepted the scientific contributions from the stranger and gave them a place in the organ of the Academy.

The Academy has for centuries continued the highest scientific body on earth; never deviating from its course to favor the fleeting fashions in the science of the day, it has ever remained mindful of the great works and inspiring teachings of its members of the past.

To have so many contributions of my own granted a place in the official organ of this body, I accept as a distinguished honor, which is still heightened by the consciousness that these contributions deviated so radically from the current teachings that they probably nowhere else would have been sufficiently comprehended to obtain recognition.

Since all those who may hereafter desire to consult the original publications on this science must turn to the Comptes Rendus de l'Académie des Sciences, it is but proper that the more detailed exposition of the subject presented in this volume, be dedicated to the Secretary of the Academy.

I therefore beg you, my dear sir, to accept this volume as an expression of the highest admiration, and as a token of the heartfelt gratitude of

THE AUTHOR.

Saint Louis, Mo., U. S.,
October 6th, 1894.

PREFACE.

The highest problem of the physical sciences is the determination of the constitution of matter. The sciences of Chemistry, physics and crystallography are equally interested and equally required in the solution of the problem of Atom-Mechanics.

Before we can proceed to the solution of any problem in mechanics we must know the distribution of the masses, as to weight and place. Accordingly, we begin Atom-Mechanics by the determination of the weight and the form of the Atoms. The solution of the first of these problems is given in the present volume.

The commonly accepted atomic weights, including those of Stas, are shown to be all in error. These errors are found due to false methods of reduction, thus leaving the direct analytical results as most important empirical data to chemistry.

Upon the false system of atomic weights has been built an equally false system of chemical science or philosophy, which has been almost universally accepted for a third of a century; it falls with the atomic weights on which it rests. In my critical exposition of these errors I have always endeavored to act in the defense of the truth, rather than to attack the error. Only where I found the truth boldly assailed by most brazen declarations of error have I allowed my pen to pierce so that the error might perish.

Having established the true and exact atomic weights, the constitution of the chemical elements as compounds of a single substance follows. The critical extermination of the fraud called the Periodic Law marks the way.

Finally, the practical consequences are concisely drawn by indicating a method of rational alchemy. The conversion of base metals into the most valuable heavy metals probably will distinguish the chemistry of the coming half century, as prominently as the organic compounds obtained by means of the autoclave have marked the half century now closing.

The work of which the present is the first—entirely independent—volume, has occupied my time during forty years. Its publication is a venture of my youngest son, who relies for success on the love of truth entertained by the general chemical public. I trust he will not be disappointed.

Gustavus Hinrichs

St. Louis, Mo., Oct. 6th, 1894.

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CONTRIBUTIONS TO ATOM-MECHANICS.

PUBLISHED IN THE COMPTES RENDUS OF THE ACADEMY OF SCIENCE OF PARIS.

FIRST SERIES.

GENERAL MECHANICS OF THE THREE STATES OF AGGREGATION.

1873: Tome 76, p. 1357; p. 1408; p. 1592.
1875: Tome 80, p. 47; p. 565; p. 766.

SECOND SERIES.

THE GENERAL RELATIONS BETWEEN BOILING POINT, PRESSURE AND ATOMIC WEIGHT AND FORM OF COMPOUNDS.

1891: Tome 112, p. 998; p. 1127; p. 1436.
1891: Tome 113, p. 36; p. 313; p. 468; p. 500; p. 743, p. 798.

THIRD SERIES.

THE GENERAL MECHANICAL EFFECTS OF CHEMICAL SUBSTITUTION.

1892: Tome 114; p. 597; p. 1015; p. 1064; p. 1113; p. 1272; p. 1367.
1892: Tome 115, p. 177; p. 239; p. 314.

FOURTH SERIES.

DETERMINATION OF THE TRUE ATOMIC WEIGHT OF THE ELEMENTS.

1892: Tome 115, p. 1074.
1893: Tome 116, p. 431; p. 695; p. 753.
1893: Tome 117, p. 663; p. 1075.
1894: Tome 118, p. 528.

I regret that the labor of re-writing this entire volume has prevented me from preparing the Fifth Series, which was to have treated of the Composition of the Elements. It will be noticed that the present volume does not relate to the first three series, but comprises the fourth series only.

SEPARATE WORKS ON ATOM-MECHANICS.

PROGRAMME DER ATOM-MECHANIK, oder, die Chemie eine Mechanik der Pan-Atome.—44 pp. 4°. Iowa City, Iowa, 1867. French Resumé of same, 4 pp. 4°, November, 1867. English Resumé, 4 pp. 4°, August 1867.

THE PRINCIPLES OF PURE CRYSTALLOGRAPHY.—pp. IV, 44, in 8°, Davenport, 1871. See especially, Chapter VI.

THE METHOD OF QUANTITATIVE INDUCTION IN PHYSICAL SCIENCE. —Davenport, 1872. See especially the last section, p. 36, giving the Mechanics of the three States of Aggregation.

THE PRINCIPLES OF CHEMISTRY AND MOLECULAR MECHANICS.—200 pp., 8°, with two plates. Cloth. Davenport and New York, 1874.

BEITRAEGE ZUR DYNAMIK DES CHEMISCHEN MOLEKUELS.—Leipzig, Gustav Fock, 1892:

I.—The Molecule as a System of Material Points.
II.—The Energy of the Molecule.
III. Graphical Structural Formulæ.
IV. The Moments of Inertia of the Molecules.
V.—The Motions of the Molecules.
VI.—The Boiling Points of Isomeric Bodies Determined by the Moment of Inertia of the Molecules.

These papers were sent to A. W. Hofmann for the DEUTSCHE CHEMISCHE GESELLSCHAFT (I, II, April, 1872; III—VI, April, 1873), of which I was a Foreign Member.

No one at Berlin did understand these papers. This very interesting and characteristic episode in the history of Atom-Mechanics is contained in the above edition of 1892.

ERRATA.

Great care has been taken to prevent typographical and other errors; while the avoidance of all such errors in so large a volume seems impossible, there has not been detected any error that is not readily recognized and corrected from the context. Thus p. 5, the departure in last column for Hg. is 0.4 as seen by table p. 4, and not 0.04 as printed. Page 77 No. 3, the weight is 200 and not 100 grammes. On page 164, the last figure in the table should be 14.041 and not 14.049, as shown by the data 161.

The letter press is very nearly free from errata. On page 30, line 8, *is* should replace *are*, and on page 204, line 3, the final e should be replaced by o to give the entire fullness to the grandissimo required by the subject.

I cannot too highly commend the intelligent care and artistic work of the printer—of which the book itself is the best evidence.

INTRODUCTION.

LAVOISIER, of immortal memory, defines as chemical elements all those substances which we have not yet been able to decompose by any means.* For over a century, chemistry has developed as the science of these Chemical Elements. In this time, a great body of well established facts has accumulated, which show that the most remarkable relations exist between these specific units of matter. From these empirical relations mechanics must determine the constitution of matter. In *Atom-Mechanics* we present the solution of this problem.

DALTON introduced the term Atom into chemical science. Upon a slender basis of established facts he boldly placed the most wonderful generalization: that chemical elements combine in fixed, simple multiple proportions only. This generalization he immediately again deduced from the hypothesis of chemical atoms, the relatively indivisible particles of the chemical elements. An entire century of chemical research has established this generalization and accredited his hypothesis.

* Lavoisier, Discours prelim., page 17.

HUMBOLDT and GAY-LUSSAC established the fact that two volumes of hydrogen gas and one volume of oxygen gas unite to form the new compound, water. GAY-LUSSAC discovered this fact of simple combining proportions by volume to extend to other gases. AVOGADRO, as early as 1811, generalized this fact. But it took the empirics of chemistry almost half a century to recognize that the law of AVOGADRO is one of the cornerstones of chemical mechanics. It practically suffices to determine which particular one of the series of exact multiples represents the simple, free particle or atom. The history of this subject has often been presented—so we need not dwell upon it here.

The first determined and most important property of the atom is its weight. Taking the weight of one atom of hydrogen as unit, we may define the *atomic-weight* of any other element as the number of hydrogen atoms required to balance one atom of the given element. (Principles Chemistry, p. 6.)

This definition raises an important question, which has been repeatedly settled by empirics, but has invariably returned to new life. The question in its oldest form is this: Will entire atoms of hydrogen suffice to weigh the atoms of all elements exactly? If so, the elements could be considered as polymeric modifications of hydrogen.

We might, therefore, expect that under certain conditions hydrogen would be converted into other elements, or the latter dissociated into hydrogen. But nothing of the kind has ever been observed or indicated, and the properties of hydrogen seem to be of an order comparable to those of the other elements. Accordingly, the so-called hypothesis of PROUT (1815) is untenable, chemically. Besides, the atomic weight of several elements, notably Chlorine and Copper, are most assuredly not exact multiples of that of hydrogen.

The definition given for the atomic weight suggests, however, a broader form of the hypothesis.

All the chemical elements, hydrogen included, might be the polymeric modifications of some primitive matter which we have called *pantogen*. If a hydrogen atom consists of two pantogen atoms, then we can weigh two atoms of all chemical elements by means of hydrogen atoms without fractions; or *the atomic weights of all chemical elements will be whole numbers*—one-half of that of hydrogen being taken as unit.

This modified form of the hypothesis of PROUT was advocated publicly by DUMAS while I was engaged in the same work, almost forty years ago. My letters addressed in 1856 to FORCHHAMMER of Copenhagen, HAIDINGER of Vienna, and to a few other distinguished scientists, are evidence of this.

A more extended paper on this subject I sent to the Physical Society of Berlin, January 26, 1857. My atomic weights system given therein was published by the Secretary, A. Krönig, as his own in 1863, in his Chemistry, and also in his "Neues Verfahren," pp. 53–60. (See Atomech, p. 3.) This small matter does not seem to have interfered in the least with the honor usually implied in such position.

The labors of the most distinguished chemists, carried on for nearly a century, have demonstrated that the atomic weights of all elements are exactly equal to these values or approach very near to the same. Without at this point expressing any opinion on this subject, we may, therefore, empirically adopt these values as "common" atomic weights. That is the values, C=12, O=16, N=14, P=31, Fe=56, Ag=108 we will call the common atomic weights of the elements specified. We selected the term "common" because these values have been in common or general use for many years, especially before the publication of the results of STAS. They are even to-day in common use in most elementary works on Chemistry, especially those published in France.

It should, however, be understood that while we have taken

H=1, we really use the sixteenth part of the atomic weight of oxygen as unit, that is, we put O=16, taking, with BERZELIUS, oxygen as the common term of comparison. Thus the actual value found for H may be either greater or less than this unit.

By means of the following table I hope to give a clear view of the changing phases of the question of the true atomic weights of the elements. The values given correspond to five distinct periods in the history of this fundamental question of chemical science. The given values refer to the identical amount of matter; only in this way can an exact comparison be made as to the degrees of approximation attained in the different times.

HISTORICAL TABLE OF ATOMIC WEIGHTS
FOR O = 16.

	Dalton. 1808.	Berzelius. 1819.	Marchand. 1847.	Stas. 1868.	Ostwald. 1891.
H	1.1	0.994	1.000	1.002	1.0032
C	11.4	12.052	12.00	.....	12.003
N	17.1	14.182	14.00	14.044	14.041
Na	.....	23.775	22.97	23.047	23.058
Mg	.	25.338	24.14	.....	24.38
P	30.9	31.384	.....	.....	31.03
S	29.8	32.186	32.00	32.074	32.063
Cl	.....	35.413	35.46	35.475	35.453
Ca	.....	40.065	40.00	.....	40.
Cu	64.0	63.31	63.44	.....	63.44
Fe	.....	54.27	56.00	.....	56.0
Ag	100.	108.128	108.00	107.930	107.938
Hg	.....	202.52	200.00	.....	200.4
Pb	190.	209.12	207.12	206.934	206.911

The mode of reduction used will best be understood from the following:

	H	C	N	O
Dalton gives	1	5	5	7
Or, equivalents	1.1	5.71	5.71	8
Hence, atom. weights	1.1	11.42	17.13	16

The values given by Dalton, 1808, in Thomson's "New System of Chemical Philosophy," are really equivalents merely. His value 7 for oxygen shows that all must be increased by one-seventh to bring it up to the oxygen standard. In order to convert these equivalents into atoms, those for C and O are doubled, that for N is trebled, while H remains unchanged. In the same manner all other values have been brought to the modern atomic standard.

A careful inspection of this table shows that only during the last fifty years results have been obtained which come quite near to definite values. It is also seen that, generally, these values are very near to whole numbers, except in the cases of chlorine and copper, which approach equally closely to the fraction of one-half exactly.

To make this as plain as possible, we represent in following table the *departures* of observation from the round or common values:

TABLE OF DEPARTURES OF THE ATOMIC WEIGHTS FROM THEIR COMMON VALUES.

Common Weight.		Marchand. 1847.	Stas. 1868.	Ostwald. 1891.
H	1.	0.000	0.002	0.003
C	12.	0.00	.....	0.003
N	14.	0.00	0.044	0.041
Na	23.	— 0.03	0.043	0.058
Mg	24.	0.14	.....	0.38
P	31.	.....	.....	0.03
S	32.	0.00	0.074	0.063
Cl	35.5	— 0.04	— 0.025	— 0.047
Ca	40.	0.00	.....	0.
Cu	63.5	— 0.06	.....	— 0.06
Fe	56.	0.00	.....	0.0
Ag	108.	0.00	— 0.07	— 0.062
Hg	200.	0.00	.....	0.04
Pb	207.	0.12	— 0.066	— 0.089

It will be noticed that there are only two values deserving special mention. The large departure for Phosphorus is evidently due to an error in the table of Marchand. The large departure for Magnesium under Ostwald appears due to error of method, and will be considered in the future.

All the other departures are small, even the apparently large one for Mercury, the atomic weight of which is very high.

This table thus clearly shows that the atomic weight of these fourteen most important elements is certainly very near the common value; but for these elements the atomic weight is among the most carefully determined.

The question now immediately arises: Are these minute departures *real*, or are they due to residual errors, experimental or mathematical, or both? This question is of the utmost importance both to practical and theoretical chemistry.

In practical chemistry we need the exact value of the atomic weights for the reduction of analyses. If we make use of atomic weights less accurate than our actual analysis, we necessarily falsify the results of the latter. If the minute departures of the School of Stas are erroneous, then all chemical analyses reduced by them have been falsified during the last quarter of a century. This would apply specially to Germany, where these Stasian atomic weights have been universally adopted.

In theoretical chemistry the consequences of such errors are still more harmful; for if these departures are not real, the atomic weights of all chemical elements are *exact* multiples of half that of hydrogen, and consequently, the elements may be considered as polymeric modifications of one substance the atomic weight of which is one-half that of hydrogen (pantogen).

The careful study of this question is the object of this first volume of my ELEMENTS ATOM-MECHANICS. I shall show that these departures are not real, but simply represent the residual errors of analysis and calculation; that the atomic weights can

be determined independently of such errors by means of my *Limit method;* and that, therefore, the chemical elements are polymeric compounds of pantogen, the atomic weight of which is half that of common hydrogen.

In order to properly present this subject—my solution of this fundamental problem of chemistry—it will be necessary to give a historic outline of the determinations of the atomic weights of the chemical elements. We shall distinguish the two great periods of progress marked by the names of Berzelius and Dumas, both of which chemists were eminent representatives of true inductive science, and worthy followers of Galilei. We shall next learn that Stas was a typical representative of the absolutely empirical state of chemical investigation that has marked the last thirty years during which chemists, and even some physicists, have acknowledged Bacon as their master. Accordingly, they have become lost in the tangles of a spurious accuracy and have succeeded in obliterating from the records of Chemistry the results of the great masters. Moreover, while analysts like Richards follow the footsteps of Stas, the mathematical chemists who have published elaborate revisions and recalculations of the atomic weights, have been mislead by the same appearances of accuracy, so that Ostwald, Clarke, Sebelien, Van der Plaats, and Thomsen have but confirmed the chemists of the past third of a century in their errors, which accordingly have gradually become fixed as tenets of faith.

We shall now proceed first to the consideration of the work of the true masters of chemical science, represented by Berzelius and Dumas; thereafter we shall closely follow Stas and his school, and show by what fata morgana they have led chemists into a desert of error. The critical part we shall cut as short as possible, and depend mainly upon positive demonstrations obtained by our methods. Finally, we intend to give the true composition of the Chemical Elements, and shall show that the dream of the old is realized: *ε'ν το παν!*

PART FIRST.

A CENTURY OF RESEARCH

ON THE

ATOMIC WEIGHTS OF THE ELEMENTS.

CHAPTER I.

THE OLD MASTERS.

Jöns Jakob Berzelius.

Berzelius had studied the subject of combining proportions as far back as 1807, especially on the lines marked out by Richter. In his Elements of Chemistry, published that year, he showed how a few good analyses would suffice to determine the exact composition of all other compounds, by a simple calculation. He accordingly resolved to carry out such a series of fundamental analyses. (Essai, p. 15-16.)

When he became acquainted with the ideas of Dalton concerning multiple proportions, he found among the great number of his analyses of which he had already the result in hand, such a confirmation of the theory of Dalton that he could not help to push the work farther. Thus the plan of his investigation was extended to the subject of combining proportions in its entirety —a subject which he found to be vastly more comprehensive than he had anticipated when beginning this work. (Essai, p. 17.)

In this field of work he spent most of his long life and accomplished the greatest success so that for over a generation he was justly looked upon as the grandmaster of chemists. His Elements of Chemistry was the standard reference book of the

chemical world and the brightest rising chemists went to his laboratory in Northern Europe to learn from the master himself what degree of accuracy it is possible to attain in quantitative chemical analysis. The great German chemists, Wöhler, brothers Rose, Mitscherlich, and others, have acknowledged their indebtedness to their Swedish master.

The earliest publications of Berzelius in which the law of Dalton really finds its first experimental demonstration, is his "Experiments concerning the fixed proportions in which the constituents of inorganic nature are found to be united."

Its first part appeared in Swedish in 1810, in German in 1811. The entire essay has recently (1892) been republished as No. 35 in "Ostwald's Klassiker" under a long-winded title which is an incorrect translation of the well chosen title of the Swedish original, which we find in Sebelien, p. 13.

The subject of multiple proportions not being under consideration, we will need to present here only some cases of determination of combining proportions, to show what degree of certainty and accuracy was attained by Berzelius at that early day in the determination of atomic weights. Our references will be the recent edition specified, the only one at hand.

The most instructive and characteristic case we can take is that of *Lead*. We shall compare the results of the determination of Berzelius with the ratios calculated from the common atomic weights Pb. =207, O=16, S=32, which give

Pb O	:	Pb	=1.0773	:	1
Pb S	:	Pb	=1.1546	:	1
Pb O_4S	:	Pb	=1.4638	:	1
Pb O_4S	:	Pb O	=1.3587	:	1
Pb O_4S	:	Pb S	=1.2677	:	1

Berzelius made five determinations of the amount of Pb O resulting from a given weight of pure lead, taking usually 10 grammes for a determination (see p. 6). The pure lead was

dissolved in nitric acid, the solution evaporated to dryness, and the residue ignited in determinations 1, 2, 3. In determinations 4 and 5 the solution was precipitated by ammonium carbonate, the precipitate filtered, washed, dried and ignited. Accordingly the last two determinations are necessarily low, (10.75 both) Berzelius properly disregards them in his final result.

The following are the weights of Pb O obtained from 10 grammes of lead:

1.	Evap. in Pt. dish	10.77
2.	Evap. in orig. glass vessel	10.775
3.	As in 2, vessel very long neck	10.78
	Adopted by Berzelius	10.775 to 10.78
	Calculated as above	10.773

It is evident from the statement of his results that he weighed to the centigramme only, in these earliest determinations; a few times we find a 5 milligramme, evidently as estimate between two centigrammes.

With this understanding as to the limit of weighing, we must acknowledge that Berzelius determined the atomic weight of lead as we now accept it, namely Pb=207. It is easily calculated that a change of one unit in this atomic weight would make a change of two centigrammes in the weight of the oxide resulting from 10 grammes of lead. This change is double the actual range in Berzelius determinations. He therefore fixed the exact entire number of the atomic weight of lead in his earliest determinations, as far back as 1810. This must be looked upon as truly marvellous, when we consider the intrinsic difficulties of the problem, and the exceedingly high atomic weight of the lead.

At the close of his first paper (l. c., p. 50), he gives another determination made with 25 grammes of lead that had been purified with especial care. He obtained, by evaporating and igniting in the same glass vessel in which the solution was effected, 25.925 grammes of Pb O. This is only 7 milligrammes less than

the value calculated from our atomic weights. A truly astonishing degree of precision.

Berzelius also made three syntheses of lead sulphide (l. c., p. 9). Ten grammes of lead gave him 11.55, 11.555 and 11.56 grammes of sulphide. The value calculated from the common atomic weights is 11.546. This differs by only one half and one centigramme from the result of the last two determinations.

He repeated these determinations afterwards (l. c., p. 48) with the specially purified lead and used also larger quantities.

Lead.	Lead Sulphide.	Calc.
25 grammes gave	28.855	28.865
15 grammes gave	17.3125	17.319
15 grammes gave	17.31	17.319

This shows that Berzelius obtained within 10, 6, 9 milligrammes the true weights, notwithstanding the fact that he operated on comparatively large amounts of substance.

Berzelius also converted the sulphide into sulphate by cauteous oxidation with aqua regia. In two determinations (l. c., p. 11) ten grammes of sulphide gave him 12.65 and 12.64 grammes of sulphate, instead of the calculated value of 12.677. The slightly greater error is simply the expression of the greater chemical difficulty of the operation.

More accurate is the conversion of the metal itself into sulphate, by dissolving it in nitric acid, and evaporating with slight excess of sulphuric acid. Berzelius obtained (l. c., p. 12) from 10 grammes of lead: a, 14.62; b, 14.635 and in c, 13.575 of sulphate from 10 of oxide, which is 14.625 for 10 of lead. Of these the only experiment completed directly is b; this gives 14.635, which is almost identical with the value 14.638 calculated from the atomic weights.

Repeating these determinations (l. c., p. 51) Berzelius obtained from 30 grammes of his specially purified lead 43.90 grammes of sulphate, corresponding to 14.633 for ten grammes

of lead; this is within 5 milligrammes of the calculated value given on opposite page.

He also converted the purest lead oxide into sulphate, (l. c., p. 51).

No.	Pb O used	$Pb\,O_4\,S$ found	Per 10 Pb O.
2	30 gr.	40.77 gr.	13.590
4	15 gr.	20.365	13.577
		mean.....	13.584
		calculated	13.587

This shows only 3 milligrammes difference on 10 grammes of lead oxide.

In his *Essai*, Paris 1819, Berzelius states (p. 144) as final result of his analyses of lead oxide, that they have given from 7.72 to 7.74 of oxide per hundred of lead. The mean of these extreme limits is 7.73, which for O=16 gives readily Pb=206.99, or only one hundredth less than 207. This is much more accurate than any of the more pretentious recent determinations. Berzelius (l. c.) adopts 7.725 as the most reasonable value; this gives Pb=207.10, which is also a very good approximation for 1819.

These few examples must suffice to furnish an idea of the manner in which Berzelius worked and the remarkably accurate results he obtained.

It is interesting to add his syntheses of silver sulphide (l. c., p. 89). The first determination gave 2.993 gr. sulphide from 2.605 gr. of silver, or 11.489 per 10 gr. of silver; in a second determination he obtained 11.49 sulphide from 10 gr. silver. For common atomic weights, Ag=108 and S=32, we have

$$Ag_2 : Ag_2S = 10 : 11.482$$

so that Berzelius also here came within the limit of his weighings.

We may add that the mean value obtained by Stas in five determinations (Sebelien p. 88) is 11.485 against the mean

11.489 of Berzelius; a difference of only 0.004 per ten or 0.0004 per unit of silver!

It need hardly be stated that Berzelius did not allow for the buoyancy of the air, or reduced his weighings to a vacuum. He was perfectly right to pronounce* it "a straining at gnats and a swallowing of camels"; for at his time the individual determinations differed more than the amount of such corrections. Besides, we shall see that, on the whole, this refinement has introduced errors of considerable magnitude, and that perfectly exact results can be obtained without resorting to the same.

The accuracy of the analyses of Berzelius being the admiration of the chemists of the world, he was requested to make known his methods of procedure. Sebelien† reports the following as the answer of Berzelius:

"Try to find that method of analysis, in which the accuracy "of the result will depend to the least extent on the skill of the "operating chemist; and when this method has been selected, "then consider what unavoidable conditions are present which "may cause errors in the result, and ascertain whether they will "increase or diminish the same. Thereafter make another de-"termination, in which exactly the opposite effects only can be "produced. If the result remains the same, the determination "was correct."

I have translated this admirable rule of Berzelius in full, because it has been forgotten, lo! these many years. But the rule is as important to-day as it was when Berzelius gave it form and governed himself accordingly. By the application of this rule fully one-half of all modern determinations of the atomic weight of the chemical elements will be thrown out from the annals of Chemistry to which they never should have been admitted; some of the "finest work" of which the present generation is particu-

* Quoted by *Sebelien* p. 45.—See Matt. xxiii. 24.
† P. 13; quoted from Gilbert's Annalen, N. F., XVIII. p. 537; 1814.

larly proud and on which the high reputation of the "*performing chemist*" largely rests, will have to be considered as if it had never been done.

Most assuredly this rule of Berzelius condemns many of the operations of *Stas* (Example, the weighing of the hygroscopic lithium chloride, Aronstein pp. 287–292) and of his most faithful followers of to-day, (Richards, Ztschr. anorg. Chem. VI, pp. 119–120; 1894).

The depth of scientific insight which characterizes the work of Berzelius is doubly remarkable because most of his special work was necessarily empirical in its nature. This is particularly the case in all his analytical work. It is therefore here that we find traces of the empiric (see pp. 49–51 of his Versuch). The most noted instance of the kind is his condemnation of Prout's hypothesis as disproved by his own analyses. See Traité, 1838, II, p. 264, where he denies the possibility of this hypothesis on the ground that his determinations of the atomic weight of lead range between 1293.17 and 1295.6, while the "multiple" of 12.5 should terminate in 87.5 and 100. But the multiple of 6.25 falls on 1293.75 which is 207 times that very number, to bring it up to Berzelius' O=100.

Berzelius used a very large unit (O=100 instead of 16) and in his later years carried out his reductions to two and three places. In the tables attached to his *Essai* of 1819, the atomic weights are uniformly given with two decimals. It is scarcely necessary to say that all these decimals are worthless; in a large number of cases even the unit is entirely uncertain. We add a few examples at random (p. 73, l. c.):

	O	P	Pt	Pb
Berzelius	100	392.30	1215.23	2589.00
"	16	31.3840	97.2184	207.1200
Common	16	31	?	207

When it is remembered that even to-day the unit place of atomic weights on the scale of O=16 in a number of cases is still in doubt, the four decimals of Berzelius' numbers resulting for O=16 are recognized as utterly worthless. Therewith falls necessarily his "experimental" condemnation of the hypothesis of Prout.

We cannot leave the period of Berzelius without calling special attention to the fact that chemistry owes its symbols and formulae, that is, its symbolism, to this great chemist, (Essai p. 109–113). This fact is too important to be ignored in our common textbooks. It is impossible to estimate the advantages that have flown from this admirable sign-language of Berzelius.—For our generic symbols, see Atomech. p. 7 and Contrib. 4, p. 48.

In conclusion we give [a smoothened transcription of G. McGowan's horrible translation of Ernst von Meyer, p. 198,] the closing words of the Memorial Oration of Heinrich Rose on Berzelius, delivered on July 3, 1851, before the Academy of Sciences at Berlin.

"When a man who is endowed with exceptional talents as an investigator enriches every branch of his science with the most pregnant facts, distinguishes himself equally in empirical and speculative research, and grasps the whole subject in a philosophical spirit; when he arranges each detail systematically and clearly, and publishes the whole in a systematic treatise, critically sifted and perfect in form; when, finally, he proves himself also a noble exemplar of a practical and theoretical teacher to a large number of disciples thirsting for knowledge—that man has so perfectly met the highest demands of his science, that he will for ages to come, remain a brilliant model."

JEAN-BAPTISTE DUMAS.

The year 1840 marks a new epoch in the history of the determination of the atomic weights of the chemical elements. On December 21, J. B. Dumas presented his "*rescarches on the true atomic weight of carbon*" to the Academy of Sciences of Paris. These researches were published in full at the head of the third series of the Annales de Chimie et de Physique, in January, 1841.

The process selected by DUMAS to determine the *true* atomic weight of carbon, is the most direct possible; namely the weighing of the product of combustion resulting from a weighed amount of carbon burnt.

He weighs the carbon—in the form of graphite or diamond—in a platinum boat; exposes it, at a white heat, to a current of pure oxygen, and absorbs the carbon dioxide so formed in a series of potassa bulbs, properly supplemented by drying tubes; the increase in weight of the absorption tubes is the weight of the carbon dioxide produced.

Great care was taken to remove all traces of carbon dioxide from the oxygen gas used; by storing the gas in a gasometer containing lime water he accomplished this object in the simplest manner.

The accurate weighing of carbon in the form of graphite was found to be practically impossible, on account of the cleavages and the pores of this form of carbon, causing more or less condensation of gases on the same. Curiously enough, chemists,

by universally combining the results obtained from graphite with those obtained from diamond, have declared it immaterial, whether the weight of the substance used is accurately known or not. Dumas has, however, kept the results obtained from the diamond separate, and specifically insists (l. c., p. 21) that "the diamond, not being porous, it has been possible to remove this error from our determinations, and we have been able to obtain a certainty in all our results which graphite did not give us to the same extent. Accordingly, out of five combustions of the diamond, there are three which give the experimental ratio 8000 to 3000 for oxygen and carbon. The two others scarcely differ therefrom." That is 16 to 12 exactly, to the thousandth of a unit.

All carbon contains some foreign matter; if fixed and incombustible, it remains after the process has been completed; and is weighed as ashes, and subtracted from the total weight used to get the real weight of carbon burnt.

Also in this regard, the diamond is the only form of carbon that should be used. Protracted boiling in aqua regia removes everything soluble; the hardness of the substance prevents all loss by mechanical handling. The ashes, as real inclusa of hard, insoluble minerals, are minute in amount and absolutely unchanged in the process.

This, together with the extreme accuracy attained by Dumas, is shown in the first combustion, of which he presents the following interesting account on page 21 of the paper mentioned.

"The first time we burnt diamond we had it weighed by a person who was a stranger to our experiments; accordingly we did not know the weight taken. We used scales of diamond, as much to try our apparatus, as to make a determination.* The combustion completed, we found 2598 of carbonic acid, from

* Hence the relatively large amount of ashes.—Hinrichs.

which we concluded that the diamond burnt weighed 708 milligrammes.* At this statement the person who had weighed the diamond was disconcerted, having put 717 milligrammes in the boat. We told him immediately, that he would find 9 milligrammes of residue in the boat, and it actually contained 9 milligrammes of fragments of Brazilian Topaz."

The following is a complete record of the results of Dumas' combustion of the diamond. All weights stated in milligrammes.

Exp.	Diamond. Number†	Weight	Ashes	Carbon	CO_2	Ratio
1	Scales	717	9	708	2598	3.6695
2	18	865	1	864	3167.5	3.6661
3	6	1221	2	1219	4465	3.6628
4	5	1233	1	1232	4517	3.6664
5	grains	1377	2	1375	5041	3.6662
					Mean.....	3.6663

This is $3\frac{3}{11}$ or exactly three-elevenths, to the fourth decimal almost, which is short only 3 ten thousandths. That is, carbon to carbon dioxide is as 3 to 11 exactly.

Hence if carbon be placed at 12 exactly carbon dioxide is 44 exactly, and for the formula CO_2 each oxygen will be 16 exactly.

Here it may suffice to say that the combustions of diamond effected immediately after this by ERDMANN and MARCHAND gave practically the same final ratio 3.6655 and H. ROSCOE in 1882, obtained, by burning over 6 grammes of diamonds from the Cape, the value 3.6660.

A detailed study of these results will be given at its proper place. Here we only wish to give an idea of the brilliant research of Dumas, made in 1840.

Two years later he presented to the Academy his "*Researches on the Composition of Water*" which were printed in full in

* Namely C: CO_2=12:44=3:11 and three elevenths of 2598 is 708½.—Hinrichs.
† Number of single diamonds used.

Vol. 8 of the Annales de Chimie et de Physique. The object of this research is the determination of the exact ratio of the atomic weights of hydrogen and oxygen.

After a careful examination of all analytical researches made for the determination of the atomic weights I emphatically declare, that these researches of Dumas are the most important of all, marking as they do, the beginning of the analysis of precision, and offering also the first—*and thus far the only*—instance of a true *series of determinations*, such as is required to furnish the absolute value of the atomic weight by our limit method. Finally, we must also admire in this work of Dumas the masterful selection of the material required, the judicious limitation of the complexity of the apparatus employed and the directness of the operations to be performed.

These two researches of Dumas will forever remain the prototypes for the experimental work required in the determination of the fundamental constants of chemistry, the atomic weights of the elements. On these two marvelous researches it has been possible to base the exact determination of the atomic weights of all elements. The two researches of Dumas on the combustion of the diamond and the synthesis of water, form the corner stone of the system of exact atomic weights.

It is a strange fact that these very researches are generally considered simply as clever analytical determinations, the pretended results of which have been found to be inexact, especially by the labors of STAS who served as assistant to Dumas during his research on carbon. And right here let us insist that the work of Stas is the best possible evidence of our statement that he was nothing but an assistant to Dumas in that first research, and had no part in the real scientific work accomplished by Dumas.

Furthermore we are bound to admit, that Dumas himself did not completely understand the far reaching bearings of his ad-

mirable process. His object was simply the determination of of the true atomic weight of carbon and hydrogen in reference to oxygen; namely C=12 and H=1 for O=16, exactly. This object he attained, consciously. But he conformed, necessarily, to the method of his day in combining, in part, the results for the diamond with those for two kinds of graphite into a general mean, and in retaining the calculation of the mean as the true value of the atomic weight sought.

No reproach can fall on Dumas for not solving the mathematical problem involved, as well as the chemical one. But it is partly owing to this fact that the results of Dumas have been practically blotted out from the annals of Chemistry, and have, for half century, been covered by a mass of conflicting data of apparently high accuracy, proceeding from his whilom assistant Stas.

Dumas has also (1859) effected admirably accurate syntheses of chloride and sulphide of silver, which we shall learn to appreciate in subsequent parts of this volume, as well as his experiments on iceland spar.

In his desire to obtain, in a short time, a great number of new determinations of atomic weights, he unfortunately, afterwards made extensive use of a method which seemed above reproach, but which must be held largely accountable for the degeneration of the science of atomic weights since 1860. This method affects also all data of Stas.

The method referred to is the volumetric silver process. Originally introduced by Gay-Lussac for the practical purpose of the wet-way assay of silver and its alloys, it was in 1845 recommended by Pelouze for the determination of atomic weights also. This method has been the object of much study by chemists. Dumas and Stas both worked in this field, and some of the finest twists have been given recently to this method by Richards in this country. Not even the modern theory of the dissociation of compounds into their so-called ions has been able to warn

chemists from this, at first rapid and ready method, which however, now* has become "hopelessly troublesome" and therefore may soon reach the happy stage of "inoccuous desuetude."

While this is not the place for argument on this point, it may be proper and convenient already here to declare categorically, that no value of an atomic weight, determined by any volumetric process, deserves to be considered other than in the light of a preliminary approximation.

But since for all elements, approximate values of their atomic weights were known before this method was applied, there was no reason for introducing it at all.

Dumas, in bending his knee to Baal, and leaving his slow but admirable processes for the quick and popular methods of the day, contributed to the unfortunate obliteration of the sense of scientific criticism, which has characterized the last thirty years of chemistry in this important field of the determination of the atomic weights of the chemical elements.

In this manner Dumas contributed himself to the subordination of his permanent and fundamental determinations to those of Stas and his school, which are of a transitory value only, like the passing fashions of a frivolous world. Not only the disciples of Stas, coolly declare the values of Dumas as of an inferior order when conflicting with those of Stas, but even Schutzenberger (p. III) in the brief éloge of his beloved master, raises Stas to the dignity of a rival of Dumas—an estimate which the impartial history of our science must consider an unintentional and involuntary insult to one of the greatest chemists of all times.

CHEMISTS OF THE OLD SCHOOL.

In this connection we must say a few words about two most meritorious German chemists, whose important labors also have

* Richards.—Ztschr. anorg. Chem. VI, p. 120; 1894.

become forgotten in their fatherland, and whose admirable results are quoted historically only to be branded as inexact and replaced by the "more accurate" results of Stas and his school. These two chemists are ERDMANN and MARCHAND.

I regret exceedingly that it has been impossible to find trustworthy data concerning the most interesting period of activity of these two great analysts, who in many regards are worthy of being called rivals of Dumas in the most honorable sense of the term. The publication of their results was subsequent to that of Dumas—and as they were published in Erdmann's own Journal für praktische Chemie, there can have been no editorial delay.

Thus, the combustion of the diamond was reported by Dumas to the Academy of Sciences of Paris on December 21, 1840; published in the first monthly number of the Annales for 1841; reprinted in Erdmann's Journal für prakt. Chemie, Vol. 23, p. 159, which is the middle volume for that year (May to Aug.). Liebig put Dumas' work in Vol. 38 and that of Erdmann and Marchand in Vol. 44. They surely followed Dumas, but so closely that their plans might have been laid independently.

The combustion of hydrogen to water was presented by Dumas to the Academy of Sciences early enough in 1842 to find a place on p. 537 of the first semi-annual volume of the Comptes Rendus. It is republished in Erdmann's Journal in the second or middle volume for the year (May to Aug.), beginning on page 456 of that volume, while on page 468 the corresponding determinations of Erdmann and Marchand are given. I gather these data from the very useful *index* to atomic weight determinations of Meyer and Seubert, Leipzig, 1883.

There are, however, several important differences between these researches of the German and French chemists, notwithstanding their rapid succession in time, their correspondence in method and remarkable concordance of results. Those of Dumas are everyway the broader and cover a wider horizon. Above all,

there is nothing in the determinations of Erdmann and Marchand resembling the regular *series* of determinations made by Dumas with greatly increasing quantities of hydrogen; and accordingly, the limit method finds in this admirable series of Dumas, the only material permitting its application to the data of one and the same analyst.

Recently the claims of S. Baup of Lausanne have been presented by W. Robert* as entitled to the credit for the determination of C:O=12:16 exactly. But his analyses of the pyrocitrate and itaconate of silver can, at best, only be used to furnish the ratio C:Ag and cannot, for a moment, be compared to the method of Dumas.

The decade so auspiciously ushered in by Dumas was remarkably rich in very good atomic weight determinations—which, however, have all been covered by the same material, so abundantly produced by the school of Stas. Hence when a good, reliable determination is wanted, it becomes necessary to go back half a century and dig out the results from under the abundant modern deposit of exact science falsely so called. We shall have frequent opportunities for such experience.

Erdmann and Marchand, already recognized, furnished excellent work on Calcium (from 1842 to 1850) and made good determinations on Iron, Copper and Mercury in 1844. They since gave determinations for Nickel, Selenium and Magnesium.

VON HAUER in 1857 made careful determinations on Cadmium, Manganese and Tellurium.

MAUMENÉ furnished a most extended series of determinations in 1846, of which especially the analyses of the organic salts of silver will prove highly important, permitting the linkage of carbon with silver.

The most important worker in what we may call the period or school of Dumas has just closed his eyes forever at Geneva,

*Bulletin Vaudoise, XXIX, pp. 192-193; 1893.

April 15, 1894. We shall soon see that the work of MARIGNAC is often superior to that of Stas, and is nearer the true values because the pertubations due to mass were less in his experiments, having almost invariably used much less amounts in his operations than the chemist of the mint of Brussels.

We cannot close this list of honor without specially expressing our approbation of the work of a chemist who apparently has long been forgotten and made determinations of one single element only; but this element, under the limited facilities for protection at the disposal of P. LOUYET, took his life as the prize of the very excellent determination of the atomic weight of fluorine, wherewith he endowed chemical science.

CHAPTER II.

STAS AND HIS SCHOOL.

JEAN-SERVAIS STAS.

We will endeavor to present a clear and just exposition of the work* of this distinguished chemist, who for a third of a century has been, and still continues to be considered as the greatest and most successful worker in the field of the determination of the atomic weights of the elements. If the determinations of a chemist differ appreciably from the results of Stas, the chemical world of to-day looks upon the new values as suspicious. If the results of Dumas, or of any other chemist of high renown, fail to agree with the values of Stas—the latter are accepted as true and the former are condemned as inaccurate, and no amount of internal evidence of perfect accuracy will save the conflicting chemist from disgracefully being showed aside as unworthy of consideration.†

Not only are the numerical values of the results of Stas universally accepted, but the philosophic inference which Stas has drawn from them, is admitted with equal readiness. We refer to the conclusion of Stas that the unity of matter is a chimera, and

* We shall quote from the translation of L. ARONSTEIN, publlshed by Quandt & Hündel, Leipzig, 1867. pp. XII, 347; 8vo.

† See Schellen, pp. 82, 99, 115, 147 and especially p. 155. The last case would be most ludicrous, if it were not an aggravating exhibition of absence of criticism. Schellen clenched his condemnation of the results of Dumas by saying that "Stas himself declares he has no doubt about the accuracy of his values."

that those who have been searching for it have been outside of the boundaries of science, and are mere speculators and dreamers.

We shall faithfully present the work of Stas and its reception by the chemical world as it stands recorded in the annals of chemical science—and shall purposely refrain from all critical remarks, leaving this important branch of our subject for a subsequent chapter of this work.

Stas had the advantage of the example of Dumas, who even mentioned the name of his assistant in the title of his research on the combustion of the diamond, in 1840. In one particular, Stas continued in the way shown him by Dumas—namely in the use of large quantities. But while these for Dumas were auxiliary and used only in a graded series, Stas made them essential and started with weights equal to those reached by Dumas at the end of his series.

While Dumas produced from about 20 to 100 grammes of water in his memorable syntheses, Stas used from 100 to 400 grammes of silver in each of his syntheses of silver nitrate. In fact, no chemist has used so large quantities, in exact analyses, as Stas has done in almost all his determinations. In his syntheses of lead nitrate and the conversion thereof into sulphate, Stas used not less than 100 grammes of lead and made two determinations with 250 grammes each.

This use of enormous quantities for exact determinations, made a great impression in favor of the results of Stas, not only on the general chemical public, but even on the mind of those specialists who have undertaken to critically reduce all atomic weight determinations made by different chemists.

Thus Clarke, after having tabulated the values obtained by Dumas in the synthesis of silver sulphide (p. 28), very forcibly conveys to the reader the impression made on his own mind by the large weights used by Stas, when saying:

"Dumas used from ten to thirty grammes of silver in each

experiment. Stas, however, in his work employed from sixty to two hundred and fifty grammes at a time."

Ostwald, the most renowned of the chemists who have carefully recalculated all of Stas' determinations, is equally forcibly impressed by the enormous quantities used by Stas. He has (p. 25–29) submitted this question to what he considers a scientific examination, from which he concludes that, in general, the accuracy of determinations are directly proportional to the quantities used. This predisposes his readers, quite at the beginning of his bulky work of over a thousand pages, to join in the opinion that in cases of differing results, those of Stas deserve the preference even on this ground alone. The use of very large quantities produced in the chemical public still another influence that, no doubt, greatly contributed to the marvelous renown of Stas. For it is impossible to use large quantities of matter in refined analytical operations except at a truly wonderful sacrifice of time, care and labor. Now this feature has not been neglected in the accounts which Stas published of his work. The time necessary for a simple operation increased from a few hours to many days; the handling of the enormous masses required the construction of special mechanical appliances; and withall, the care of Stas was so extraordinary, that his weighings agreed almost to the milligramme on these enormous masses, after having subjected them to complex chemical and physical operations. The effect produced on the chemical mind of the world was stupendous, crushing—it was a true effect of mass in the chemical sense.

A very special feature in the work of Stas is the "*complete*" synthesis or analysis. He weighs each ingredient separately, also the product obtained; and finds this to be almost identic with the sum of the weights of the constituents used. This process would seem to absolutely exclude the possibility of error. In this manner he effected complete syntheses of silver iodide

and silver bromide. He also made two complete analyses of silver iodate, collecting and weighing the oxygen produced by the dissociation of the iodate, as well as weighing the iodate used and the iodide remaining.

Another much admired special feature of the work of Stas is the repetition of a given determination according to different methods and by the use of materials produced by different processes. Yet, under these varied conditions, the results obtained were almost identical. Thus, the ammonium chloride he used, he prepared according to four different methods (pp. 49–60); silver iodate he prepared in four different ways also (pp. 61–76); the synthesis of silver chloride he effected according to four different processes (pp. 171–176); etc., etc. In addition he used the utmost care in the selection and construction of all the apparatus he employed. His special study of glass, as to its power of resistance to chemicals under the specific conditions of his experiments, has become famous.

In weighing, he not only employed all customary artifices in using counterpoises like the vessel actually employed, and allowing for the buoyancy of the air as exerted upon the body weighed —but he also took into account the buoyant effect of the air on the weights themselves (Sebelien, p. 50).

We have not room for further details on this subject. What has been said will suffice to make the reader understand how the publication of the papers of Stas in 1860 and 1865 took the chemical world as it were by storm. The entire chemical literature of the past third of a century can be used to supplement what we have said here.

But besides all this, there was still another very potent element for admiration in the work of Stas—not experimental, but mathematical.

Stas takes it for granted that if potassium chlorate is dissociated, the residue left in potassium chloride, and the loss is

oxygen—save the trifling corrections which he aims to determine by experiment.

Potassium chloride he again uses to precipitate a silver solution, and thus connects its atomic weight with that of silver. It is *this system of complex relations*, requiring actual algebraical elimination, that has lent as great a charm to the mathematical side of the determinations of Stas, as his immense quantities gave to their purely chemical features.

Why, his entire research, extending over years of labor, might have been completed, without calculating a single atomic weight; and as has been done by Clarke, Ostwald, Van der Plaats and Thomsen, the experimental results might, years afterward, be put into a series of equations, the mathematical solution of which would give all the atomic weights involved, any one depending on all the others.

While all this seemed to be amply sufficient to stamp the results of Stas as experimentally and mathematically beyond question, STAS went one step further—apparently the only step still possible—and determined, by the refined methods of the calculus of probabilities, the possibility of errors of any definite magnitude in his final results. While he published such a calculation for his values of nitrogen only, (pp. 322–323), the impression conveyed and received is that the accuracy of the other atomic weights is of an order like that of the one considered. To do full justice to this important phase of the atomic weights of Stas, I shall transcribe the entire passage:

"The atomic weight of nitrogen is therefore 14.045 with a mean error not exceeding 1/4000; it has been determined from the proportions of the chlorides and nitrates of *four* metals, of which *three* belong to the best known of all elements.

"My older syntheses of silver nitrate led me to the mean 14.040

"My new syntheses of silver nitrate give (Ag=107.93) the mean 14.042

General mean 14.044

"Subjecting these data to the calculus of probabilities, we obtain the following results:

"If the general mean is	14.044
"Then the sum of the squares of the errors is	0.000 034

"Which gives for:

The mean error of one determination	0.002 601 683
For the probable error of one determination	0.001 758 854
For the mean error of the mean	0.001 062 134
For the probable error of the mean	0.000 718 0485
Measure of Precision of Mean	H=665.7423

"The probability that the mean 14.044 is as much as x in error to the true value of the result, is determined by the formula

$$y = \frac{H}{\sqrt{\pi}} \cdot e^{-H^2x^2}$$

wherein π is the ratio of the circumference to the diameter and e the base of the Neperian Logarithms.

"Accordingly, the probability that the true value amounts to

14 040 is . . .	y=0.31278	
14.030 " . . .	y=0.0	.0 (35 ciphers) 701
14.020 " . . .	y=0.0 .	0 (108 ciphers) 505
14.010 " . . .	y=0.0 .	.0 (219 ciphers) 115
14.000 " . . .	y=0.0 .	0 (370 ciphers) 879

"Accordingly, the value 14.040 is *possible*, since its chances are 3 in 10; the value 14.030 is already extremely improbable, and the others must be considered as absolutely impossible.

"These researches show sufficiently, that the value 14.00, which at present is accepted by almost all chemists as the representative of the atomic weight of nitrogen, is inexact, if oxygen is put at 16.00. The number 14.00 is in error to the extent of 1/350."

Nothing can be more learned, nothing can be more absolute —and chemists bowed in admiration, adopting the dictum of their accepted master.

In closing his great work, STAS expressed modestly a request —really challenged the chemists of the world—in the following manner, as to the experimental data he had furnished (p. 347):

"At the close of this extended work I ask permission to express a wish: namely, that a chemist, whose reputation is sufficiently established, would please take the trouble to control (i. e. re-determine) one of the fundamental numbers of my researches for example, that of the synthesis of silver nitrate, and to publish the result of his research. Without reserve, I shall submit to his judgment."

As a matter of fact, no one has accepted this challenge, and STAS has accordingly renewed the same in his last memoir of 1882.*

It is not necessary to give special values and examples of the work of Stas in detail—the entire modern chemical literature is but a representation hereof. It will suffice to print the values of the atomic weights given by STAS himself in his three publications of 1860, 1865 and 1882. I copy from Van der Plaats, p. 531.

THE ATOMIC WEIGHTS OF STAS.

	1860.	1865.	1882.
Ag	107.943	107.930	107.9300
Cl	35.46	35.457	.....
Br	.....	79.952	.....
Io	.....	126.850	.....
S	32.0742	.....	.....
Ka	39.13	39.137	39.1425
Na	23.046	23.043	23.0455
Li	.....	7.022	.....
N	14.041	14.044	14.0550
Pb {	206.906 Sulphate.		
	206.920 Nitrate.		

* See Van der Plaats, p. 518, referring to γ, 65.

Let us now try to convey to the reader an idea of the reception and appreciation of the work of Stas by the chemical world. The Royal Society of London bestowed upon Stas the Davy-Medal in 1885, for the following reasons, as expressed by the president of that society:*

"Professor Stas' great research for which it is proposed that the Davy-Medal be awarded to him, is that on *atomic weights.* There are probably no researches in chemistry, the results of which appeal so little to the imagination, and which are so little applauded as those on atomic weights, yet for difficulty and importance, they are hardly surpassed by any.

"The indefatigable and conscientious care which M. Stas has devoted to the re-determation of a certain number of the most important atomic weights, and the marvelous skill with which he has overcome the various difficulties which successively presented themselves, render his Memoir on the subject one of the most remarkable and valuable of chemical monographs."

The most concise expression of the appreciation of the chemical world of the work of Stas is found in the pages of the "*Manifestation*" issued to give an account of the celebration of the fiftieth anniversary of his election to the Academy of Sciences of Brussels. This celebration took place on May 5, 1891. We copy the following expressions from the pages of this publication.

Professor A. Kekulé, as president of the German Chemical Society of Berlin, says on behalf of this Society in his address to Stas of May 1, 1891, (p. 64):

"The acuteness and indefatigable care which you exhibit in the execution of your labors (on atomic weights) will for all time to come serve as a Model to Chemists. The principal questions in this field have been settled thereby, and in such a way

* Stas' Manifestation, pp. 3, 4; quoted from Proceedings Royal Society, Vol. XXXIX; 1886.

that not the slightest doubt can remain about the truth of the results which you have obtained. Thus it has happened that the wish, which you expressed at the close of your work, that a chemist of renown might test any one of your fundamental numbers, has not been fulfilled, for everybody was from the first fully convinced, that he would find exactly the same values again; this is an evidence of the high recognition which has been bestowed upon your labors."

The Chemical Society of London sent an address, signed by Crum-Brown, Crookes, Frankland, Roscoe, Thorpe and other noted members. We copy the following important passages from this address:

"A most important result of your inquiries has been the refutation, in its original form at least, of the famous hypothesis of Prout, your marvelously accurate determinations showing, that it is no longer possible to believe, that the atomic weights of the elements are expressible as a series of multiple whole numbers, (p. 73)."

"Hence your researches on the reciprocal proportions of the atomic weights must be handed down to future generations as one of the most valuable classics of the Exact Sciences," (p. 74).

The Academy of Sciences of Amsterdam sends an address from which the following passage (pp. 77, 78) deserves a place here:

"That which in your work has particularly struck us is the high scientific spirit which guides you in all the applications which chemistry calls for. But that which in our opinion constitutes your Monumentum Aere Perennius, are your researches on the mutual relations of the atomic weights. You have yourself recognized the extreme importance of this subject, by repeating your analyses with truly extraordinary carefulness and extreme expenditure of time. . . . You have with a sure hand traced the line of demarcation between "experiment, measure, and calculation" on the one hand, and purely mental

conceptions on the other. . . . The basis of the sciences of nature is their method, and by insisting most vigorously on the duty of maintaining this method, you have rendered science a most valuable service."

The "Redaktion" of the "*Jahresbericht der Chemie*"* sends a very positive and very ponderous address, signed by the fourteen editors of that peculiar institution, (pp. 66, 67). I do not dare to omit anything from the declaration of the Areopagus of German Chemistry, and accordingly give their address in full:

"By a most conscientious investigation on the laws of the chemical proportions, carried out with the most painstaking care, you have discovered in the years 1865, '66, '67, (sic.) one of the most important facts which ever enriched the *field* of our science in the *field* of exact investigation, especially that of Chemistry. You have demonstrated to be erroneous the then generally, after the example of Dumas, accepted hypothesis of Prout, according to which the atomic weights of the elements are *simple* multiples† of that of hydrogen (=I) or respectively of the number 0.5 or 0.25; you have shown by extremely accurate observations, that the *combining capacity* of the elements *does not rest on such a flat basis*, but on the contrary *progresses* according to laws and rules which leave still open a wide field for *our* investigations. At the same time you have shown in that work of genius, that the *ability of the elements to enter into reaction* with a definite combining-weight, is one that rests upon an unchangeable *basis*, and that a transformation of one compound into another is possible without the *slightest* loss in mass, as well as that temperature and pressure exert not the *slightest* influ-

* Ever since (1869) members of this areopagus have used this Report for by wholesale condemnation to prevent chemists to examine new investigations, in order to publish them as their own, a few years later, I have tried to get along without this degenerate successor of the Reports of Berzelius and Liebig. In the days of the masters, the Report was moderate in size, and as honorable as it was reliable; since it has become bulky and bad. The German chemists who pride themselves on their reading by relying on the Jahresbericht often make a sorry show of themselves before those who have examined the originals "reported" upon.

† Lead would be the very *simple* multiple of 207, 414 or 828!

ence on the composition of definite chemical compounds and that accordingly the relations of weights of the elements, which compose them, are altogether unchangeable.

"By this fundamental work you have given to chemical investigations a *new direction*, you have revealed a high confidence in her method of analysis and synthesis, and *have elevated chemistry to the rank of the most exact science in the field of natural phenomena.* This act of yours, the chemical world has not yet forgotten to-day, and never will forget that it owes it to you. Accept therefore, highly honored Sir and Jubilar, the most sincere and cordial felicitations to your *day* of Jubilee of this *day* from the REDAKTION of the Jahresbericht der Chemie, in which friendly join the gentlemen collaborators whose names are also signed.

Hochachtungsvollst und ergebenst,

Prof. Dr. F. FITTICA, Redacteur,
and 13 other signatures.

I have taken great care in the translation of this in every way most remarkable document professedly representing German Chemistry. Such a pronunciamento, from such a quarter, deserves all the place it occupies here, and should be carefully studied by every reader. As Professor Dr. Fittica declares the opinion of the entire chemical world of the present and of all future time, we are bound to listen attentively, and make a note of it—even if it be hard to infer that he has understood himself or has ever carefully studied that which he extolls so highly.

As a relief, we will add the clear and positive opinion of Professor Ostwald (l. c., p. 129) which in a most characteristic manner exhibits the habit of the school of Stas of imparting con amore an occasional kick to the dead lion—Dumas.

"Quite another way traveled the co-laborer of Dumas from the work on the combustion of the diamond they had effected. Also he (Stas) set himself the problem to decide the question by

the most exact determination of a few atomic weights, and also he began, according to his own statement, with the conviction of the truth of Prout's hypothesis. But while Dumas "with that hastiness of reasoning peculiar to him" (Berzelius), concluded the correctness of the preconceived opinion from numbers, the inaccuracy of which a subsequent test in many cases revealed, Stas presented in his labors the never before attained model of reproachless atomic weight determinations which form the basis of our present knowledge of these constants, and he (Stas) drew from these results the conclusion, that the hypothesis of Prout is nothing but a *chimera.*"

Corresponding to this, Professor H. LANDOLT begins a paper presented to the Academy of Sciences of Berlin* and reprinted at the head of the twelfth volume of Ostwaldt's Zeitschr. f. physik. Chemie, with the following thoroughly characteristic words:

"*It is well known* (Bekanntlich) that the old hypothesis of Prout, according to which the atomic weights of all elements are to be entire multiples of that of hydrogen, *has been completely disproved* by the labors of Stas and Marignac,† as well as by many later determinations of atomic weights." Then he absurdly gives the Mayer-Seubert values to show the "considerable" deviations from the whole numbers. How blind faith in authority has dwarfed the chemists occupying high places!

I believe that I have faithfully explained the essential points in the great research of Stas, and equally faithfully have shown how almost from the start and till the very present chemical authority has been absolutely and unreservedly in favor of his results and his work.

Such has been the opinion of the past, and such it is at present. The judgment of the future will depend solely upon truth and real merit.

* Sitzungsber. 1893, pp. 301-334.
† Marignac does not belong there for he did oppose Stas.

REVISORS AND RECALCULATORS.

OSTWALD, CLARKE; SEBELIEN, VAN DER PLAATS, THOMSEN; BECKER, MEYER AND SEUBERT.

It would seem that the determination of the atomic weights of the elements had been completed in its essential points, and only would require some additional work of detail. The unqualified acceptance by the chemical world of the work of Stas ought to imply nothing less. Nevertheless, the last dozen years have brought quite a series of special treatises, averaging 200 pages each, supplementing and revising especially the calculations of Stas.

The list of names at the head of this section shows both the extent and the weight of this new work. It seems that, after receiving the investigations of Stas with acclaim, as recorded in the first half of this chapter, the more thoughtful chemists felt not quite satisfied therewith. Not only is the mathematical treatment of the data of observation in the publication of Stas exceedingly incomplete, but when his experiments, for which extreme accuracy is universally claimed, were subjected to systematic re-calculation, the final values obtained did not agree to a corresponding extent with those given by Stas. Even Stas

himself has given three sets of different values, namely one each in 1860, 1865 and 1882, exhibiting changes in the second decimal. (See above p. 34.)

For example, the value of the atomic weight of nitrogen which had been fixed with such wondrous accuracy at 14.044 in 1865, was by Stas in 1882 coolly put at 14.055, which differs by a full hundreth therefrom. By his most elaborate and crushing application of the calculus of probabilities, such a difference had been proved impossible by himself in 1865. He records it, however, in 1882, without any remarks, and the admiring chemical world seems not to have noticed this slight of hand.

It would be quite interesting to consider the subject of the mathematical revision and recalculation of the experimental determinations of Stas in detail; but space will not allow more than a brief exposition of the entire subject and a general characterization of each one of the attempts made.

On the whole it appears, that only methods of calculation have been bodily carried into chemistry from other fields of science, notwithstanding the fact, that the problem to be solved, being a specific chemical one, necessarily would seem to demand equally specific methods of calculation.

Two of these revisions are more pretentious in form than the others, for they submit the determinations of Stas to the refined *method of the least squares* and give the *probable error** of each mean taken. These most thorough chemical calculators are Clarke of Washington and Ostwald of Leipzig. To judge of the value of their work, we will present a prominent example from each one of these distinguished authors and pronounced admirers of Stas.

* For an experimental investigat'on of this subject, I beg leave to refer to my *School-Laboratory*, Vol. II., p. 28-38; 1872, and especially to pp. 43-56 of my RAINFALL LAWS, deduced from twenty years of observation. Washington, 1893. I have had made by my students, more than half a million determinations on this subject of probabilities.

For applications hereof to theoretrical chemistry, see my *Principles*, pp. 133-137 and 163-165.

Wilhelm Ostwald.

The first determination of Ostwald,* on which all his other values rest, is that of the atomic weight of potassium chloride, which he finds, for O=16, to be 74.5902 with a probable error of 0.0045 (l. c., p. 31). That means, the real value of KaCl may reach as high as 74.5947 and fall as low as 74.5857. Furthermore these limits are the only ones admitted in all subsequent calculations of Ostwald; hence, this mean and its probable error affect all other values determined from the analyses of Stas by this calculator.

The following are the data used by Ostwald representing the atomic weight of KaCl calculated from the analyses of Stas of potassium chlorate in the dry and wet way (l. c., p. 31).

No.	Dry Way.	No.	Wet Way.
1	74.5681	6	74.6060
2	.5716	7	.6143
3	.5860	8	.5862
4	.5968		
5	.5895		
Mean	74.5815		74.6022
Range	.0287		.0281

Nothing more is necessary than the mere tabulation of these numbers-- given by Ostwald himself at the place stated in his big work on General Chemistry to prove that this distinguished chemist is on ground where he is not at home. He evidently has no idea of the serious blunder he makes; his exclusively chemical students and readers no doubt admire the show of mathema-

*Lehrbuch der allgemeinen Chemie. Band 1: Stöchiometrie. Zweite Auflage. Leipzig, Engelman, 1891, pp. 1164, 8vo. The part here under consideration in Book first pp. 1-138. The first edition appeared 1884.

tical thoroughness presented; but those familiar, not only with the mere mechanism of the calculation, but also with the necessary conditions and limitations of this method employed, must stand aghast.

Let us examine into this fundamental step in the calculation by Ostwald, of the atomic weights of all the elements. If we can show that this first step, the basis on which all the others depend, is in error, and even absurdly so, we may be excused from spending further time on the balance of the atomic weights of Ostwald.

Now, in the first place, the three determinations in the wet way give a mean which is 0.0207 in excess of the mean of the five determinations in the dry way. In other words, the actual difference of the means of the two series amounts to more than four times the probable error of the mean of Ostwald. To assert that the probable error of the mean KaCl=74.5902 is only 0.0045 is therefore contrary to the most patent facts in the case.

Furthermore, the real chemical uncertainty of these determinations is the entire range, from the least to the highest value actually found. That is

greatest, wet way	74.6143
lowest, dry way	.5681
Total Range	0.0462

which amounts to more than ten times the "probable error" given by Ostwald.

The mathematical absurdity of this entire calculation of Ostwald is plainly shown by the differences of the individual determinations from the mean given by him. For the sake of brevity, we express these differences in units of the fourth place. They are readily obtained by simple subtraction, and are as follows:

No.	1	2	3	4	5	6	7	8
Diff.	-221	-186	-43	66	-7	158	241	-40

of a *mean* value; for they vary systematically with the absolute quantities used, as I have shown (C. R. T. 115, p. 1074; 1892.) We shall come back to this important subject.

To complete this topic we add the values found by Ostwald, together with the charmingly small "probable errors" which he has calculated. (l. c., p. 42). If these results were reliable, the question of the true value of the atomic weights of the elements might well be considered closed, and the unity of matter definitely disproved—a chemical chimera.

Metals.	Atomic Weight.	Probable Error.	Metalloids.	Atomic Weight.	Probable Error.
Ag	107.9376	0.0037	Cl	35.4529	37
Ka	39.1361	32	Br	79.9628	32
Na	23.0575	41	Io	126.8640	35
Li	7.0303	42	S	32.0626	42
Pb	206.911	90	N	14.0410	37

This "probable error" amounts to about four thousandths or less in all cases except that of lead. The second decimal should therefore be certain, the uncertainty being less than half a hundredth. But, unfortunately, not one of these values has been obtained by legitimate mathematical processes. The entire list of Ostwald's numbers is therefore without scientific value; it possesses interest solely as an instructive curiosity in the history of chemistry. It marks the decadence of scientific chemistry in Germany, the necessary result of blind authority worship.

Frank Wigglesworth Clarke.

This recalculation* of the atomic weights was made while Mr. Clarke was professor of Chemistry at the University of Cincinnati. It has been published by the Smithsonian Institution at Washington in 1882. This book will remain of permanent value, because it gives, in a large number of cases,† the results of the actual, individual weighings (reduced to vacuum) made by the analysts. So far as I have had occasion to examine the experimental data, I can testify to the accuracy of the record given—a result requiring extraordinary carefulness, considering the great number of data recorded.

It is to be regretted that Professor Clarke adopted the *unknown* hydrogen unit, in which he puts oxygen at 16.96; but he converts the final results always to the Berzelian oxygen unit, taken at O=16.

The special values obtained by Clarke are all affected by his method of calculation used, which is unique, and apparently theoretically perfect, when considered from an exclusively mathematical standpoint. He determines, by the method of the least squares, the probable error of the mean for each series of deter-

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* A Recalculation of the Atomic Weights. By Frank Wigglesworth Clarke, S. B., Washington: Smithsonian Institution, 1882. pp. XIV, 279, 8vo. (Smithsonian Miscellaneous Collections, No. 441). Also, under the Title: The Constants of Nature, Part V.

† In many important cases this has been omitted, as for example in the syntheses of lead sulphate and nitrate, pp. 73-76—an omission which is very serious on account of the fundamental importance of these syntheses. Stas' weighings have, quite generally, not been given by Clarke.

minations made; then he combines all series into one by the well known formulae, and calculates the probable error of the resulting atomic weight.

Chemically, these final results are of very little value; for in most cases, the number of determinations made in any one series is so small that the application of the method of the least squares is not justified; besides, the most important, really chemical errors, cannot show up at all in this process—as Clarke himself knows perfectly well—see his exclusion of series 2, 4, 5 of lead, below.

But if we, for the sake of company, were to adopt the mean of a number of determinations of atomic weights as the most probable value, and were to combine the different means according to the method adopted—we would, no doubt, obtain the values given by Clarke; for his work of calculation has been done with much care.

The actual existence of constant and other chemical errors, and the fact that in very few series the total number of determinations warrants the use of the method adopted, precludes the possibility that the final results can have weight as chemical constants. Not one of them is a *Constant of Nature.*

As an example, we select the case of lead, in which the number of determinations is favorable, being rather large in several series. Clarke states his final result (l. c., p. 77) in the following manner:

"We have seven ratios upon which to base our computations:

(1) Per cent. of Pb in PbO, 92.8271 ± .0013

(2) Per cent. of PbO in PbN_2O_6, 67.4016 ± .0014

(3) Pb : $PbSO_4$ :: 100 : 146.4262 ± .0023

(4) PbO : $PbSO_4$ :: 100 : 135.804 ± .018

(5) $PbSO_4$: PbN_2O_6 :: 100 : 109.307 ± .002

(6) Pb : PbN_2O_6 :: 100 : 150.9704 ± .0010

(7) Ag : $PbCl_2$ :: 100 : 120.7266 ± 0.013

From which Professor Clarke obtains:

Series.	No. Determ.	Atomic Wght.	Prob. Error.
1	9	206.587	0.059
2	4	7.046	41
3	13	6.435	41
4	7	7.131	118
5	3	4.803	329
6	10	6.454	37
7	4	6.473	42
"General mean		206.604	0.019
If O=16, this becomes		Pb=207.079	

"In the above discussion are included several values which diverge widely from this general mean, and which, for other reasons, are probably erroneous. Although but one of these carries much weight, it is well to exclude them, and to base our computations upon the others. If, now, we reject the second, fourth and fifth values, we get for the atomic weight of lead, Pb=206.471 $\pm$ 0.021. If O=16, this becomes Pb=206.946.

"From the synthesis of the nitrate Stas found 206.918 and from the sulphate 206.934. The agreement of these values with our own general mean is certainly very close."

We have given this much space to the revision of Clarke, in order that the apparent advantages, as well as the inherent weakness of the system, might be more fully appreciated. The instance selected sets forth both in a strong light. We also notice that Clarke is a pronounced Stasian—he still declares himself so in a recent letter. However, to justly represent him, we think it proper to copy the closing words of his book, (pp. 270–271):

"I began this recalculation of the atomic weights with a strong prejudice against Prout's hypothesis, but the facts, as they came before me, have forced me to give it a very respectful consideration. All chemists must at least admit that the strife over it is not yet ended, and that its opponents cannot thus far claim a perfect victory."

JOHN SEBELIEN.

With reminiscences from the early days of Atom-Mechanics.

The University of Copenhagen offered, in December, 1881, its gold-medal for "a historico-critical exposition of the experiments, by which the atomic weights of the elements have been determined."

The prize was awarded to the author of a paper bearing as motto the noted word of Newton: "*Hypotheses non fingo.*"

This paper has been published* in German in 1884, by its author, John Sebelien, now professor of chemistry at Aas near Christiania, in Norway. It is a most valuable work, rich in experimental data gathered from the annals of Chemistry, and as such, fully deserves the recognition it received from the old University of the Athens of the North. While a few errors in the numerical values, in the absence of corroborative data, have given me much needless trouble, I take pleasure in testifying to the high merit of this historical essay. It is very useful, especially to the investigator in the wilderness, on account of its rich and complete references and quotations, as well as its abundance of numerical data.

Most assuredly, Sebelien has been faithful to his motto. But it is greatly to be regretted, that he has done much worse than invent hypotheses. He has persistently, we do not say willfully, misrepresented facts, and manifested an unjustifiable bias against Dumas and in favor of Stas (p. 82, 99, 115, 147, 155, etc.) The

* Beiträge zur Geschichte der Atomgewichte. Von John Sebelien. Eine von der Universität zu Kopenhagen gekrönte Preisschrift. Braunschweig, Vieweg und Sohn, 1884. pp. VIII, 208, 8vo.

first is a much graver offense than the invention of a hypothesis; it is also much easier to commit, and at times more sure of a speedy reward.

The chemical atmosphere from which the question emanated, had probably a high Stasian tension. Though the question does not refer to Stas or Prout, but is aimed to be altogether objective, Sebelien, in his preface, volunteers the statement, that the *main result* of his labor had been established by him already in August 1882, three months in advance of the time limit fixed by the University. This main result is declared to be the insufficiency of the hypothesis of Prout, about which the University really had asked no question at all. However, it granted the prize and the amount of labor performed merited the recognition, notwithstanding the fact that the "main result" accentuated by the author has no existence outside of his own imagination, and possibly the imagination of his judges and professors.

How happy is man, when he takes the oars in, sets his sail to the wind, and, reclining comfortably in his little boat, judiciously limits his exertions to a slight pressure on the rudder, sufficient to keep the sail well filled with the wind, whatever be its direction! The Vikings of old did not conquer the world in that way—they were men of daring and determination; but they are, mostly, dead now.

However, time will tell, and after we have held back the impetuous young worker and perhaps placed apparently insurmountable obstacles in his way, we gradually learn* "with a more unbiased eye, to look upon the great riddles which nature presents to science."

And it also is very true, that "during the last twenty years, the relations between the properties and the atomic weights of substances, have been inquired into from diverse quarters" (l. c., p. 23).

* Julius Thomsen, Om Materiens Enhed. Copenhagen, 1887. p. 38.

This lapse of time brings us down to 1867, the very year in which copies of my *Programme* of Atom-Mechanics were sent back to Copenhagen. I may add, that a dozen years earlier still, there was a student in the Polytechnic School of Copenhagen, who had already at that time, reached far beyond the stage of science represented and acknowledged by the actual director of that school in his learned address before the University of Copenhagen on April 15th, 1887, i Anledning af Hans Majestæt Kongens Födselsdag.

It is one of the great mysteries of the world, that resistance developes mental, and strengthens physical power in a healthy man. I am, therefore, profoundly thankful to men in my old science home, for their kindly exertions in this direction, and trust that I have not enjoyed these prizeless opportunities without being greatly benefited by them. However, I am sure, I retain only the kindliest recollections in my mind; whatever else there may have been, has long ago faded out entirely.

This rather general and somewhat personal review of the excellent compilation of Sebelien, must suffice for the present. We shall, in the future, draw again upon the storehouse of data which he has gathered from many quarters, and which in themselves are abundantly sufficient to demonstrate, beyond a doubt, that *the atomic weights of all the elements are exact multiples of half the atomic weight of hydrogen*—although Sebelien himself professedly arrives at the opposite conclusion, and has been rewarded by the University of Copenhagen, for obtaining so desirable a result.

How useful such a book would have been to me, almost forty years ago, when, before I knew of Prout and of Dumas, I presented the above as a hypothesis to the director of the Polytechnic School of Copenhagen, Johann Georg Forchhammer,* who most kindly and attentively listened to me.

*He was not by birth a Dane, for he was born in my own native province, Schleswig-Holstein.

At the World's Fair in Chicago, 1893, I was delighted with the beautiful exhibit made by little Denmark. The magnificent three-towered front of the exhibit was constantly crowded, the multitude admiring the prominently placed statues of the two apostles of beauty, which Denmark has given to the whole world: Albert Thorwaldsen, the master in marble, and Hans Christian Andersen, the master in fancy.

The right wall, on the outside, toward a narrow alley, was decorated with large well painted landscapes, representing actual views in that beautiful little garden in the sea:

> Danmark, deiligst Vang og Vänge,
> Lukt med Bölgen blaa!

High up on this wall, above these portrait-views from the green beech woods of Fyen and the white chalk cliffs of Möen, almost hidden from the throng, but instantly recognized by the eager eye of the disciple, were placed the bronze busts of the two most distinquished scientists which Denmark has produced during this century—Oersted and Forchhammer.

Beholding the life-like features of the teacher, who introduced me to the science that has without ceasing fascinated me, I seemed to hear once more his kind voice of forty years ago, asking me again, as he did then in his study, how I was getting along in my work.

At that far away time I confessed to him, that I found difficulties in his own chemistry only, in the multitude of unconnected facts and the absence of deductive reasoning from general principles; that, while deeply interested in his lectures and experiments, I was mortified at the apparent impossibility of my ever *understanding* that science, while physics and mathematics gave me no trouble whatever.

He seemed much interested at my blunt confession and explained, that it was not possible to treat chemistry like physics or mathematics, because it was an experimental science.

"But it must be possible, it ought to be *made* possible," I rejoined—for which outburst I was rewarded by one of his most benign smiles, and an apparently greatly increased interest in myself.

Less than a year after that conversation, I presented to him, for his consideration, a sketch of the first scientific contribution I ever made. It had for a basis the *hypothesis* of a single primitive substance, all atoms of which, therefore, were exactly equal; and I made the attempt to deduce the varied properties of the different chemical elements from the differences in *weight and* FORM of their complex atoms, built up from the equal atoms of that primitive substance. This was in February, 1855.

Ever since that day I have labored faithfully, to rigorously test and develop that hypothesis, and to make general chemistry a mechanics of the atoms; this labor now has continued almost forty years, and has never been much interrupted by even the most adverse conditions.

The native of a war-stained borderland became the victim of contending forces and was compelled to make a new start in a new country, where but too often the highest interests are at the mercy of some brutal and ignorant political dictator or some sanctimonious hypocrite;* I had to meet the combined deviltry of both.

To formulate a hypothesis and to spend a life of labor in testing the same, endeavoring to connect it by solid bars of rigid mathematical processes with the results of the best made, criti-

* These powers of DARKEST AMERICA did not accomplish my ruin, but found themselves the subject of a legislative investigation and removal. However, united with the Military Weather Bureau at Washington, they did cause the destruction of my Meteorological Observatory, and the greater part of my scientific work connected therewith. The "Military" Weather Bureau was ended 1891.—About three centuries ago, a kindred brood destroyed the grandest astronomical observatory the world had seen till that time; but the great builder of Uraniborg truly said:

Undique terra infra, coelum patet undique supra
Et patria est forti quælibet ora viro.

cally checked, experiments; this has been the main work of my entire scientific existence. And though a scientific pharisee may, and a blind empiric will, look upon such work with a scornful eye, they should not take that famous word from NEWTON as a motto; for the scientific life of Newton himself was largely made up of exactly that kind of work!

"HYPOTHESES NON FINGO," says Sebelien, as the representative of a large class of modern empirics—and then proceeds to distort the observed facts into a contradiction of the great law of which these facts are the expression, and a famous University crowns his work with its gold! It is always a dangerous undertaking for our modern specialist, who knows so much about a very little, that he thinks there is nothing outside of that little worth knowing, to apply a scientific tool, borrowed from other fields, for the purpose of disproving any great scientific principle whatsoever; for their mind is no more able to handle great laws of nature, than a beggar would be able to judiciously handle the great sums of a banking house.

But above all, the empiric should not boast and rejoice that he is not so reproachful a worker in science as the inventor of hypotheses; for that has been condemned by the great teacher* long ago.

* I quote from memory and crave pardon if I fail to reproduce the grand lesson, Ev. Lucæ, XVIII, in every particular:

10. Homines duo ascenderunt in templum ad orandum; unus Pharisæus, et alter publicanus.

11. Pharisæus stans apud seipsum haec orabat: Deus, gratias ago tibi, quod non sum, sicut reliqui homines, aut etiam, sicut hic publicanus.

12. Hypotheses non fingo.

13. At publicanus procul stans, non voluit ne quidem ocolos in coelum atollere: sed pulsauit pectus suum, dicens: Deus, propitius esto mihi peccatori.

J. D. Van der Plaats.

"Chemistry of precision is a science of the Laboratory; it has nothing to do with the art of grouping the figures."

This statement of Van der Plaats, Professor of Veterinary Chemistry at Utrecht, in Holland, was made by him in the Comptes Rendus (T. 116, p. 1367; 1893) only a year ago, when he presented his *second* and *third* series of "figures" pretending to represent the final results of the *atomic weights* which he by calculation had extracted from the analytical determinations of Stas; and this after the same Van der Plaats, seven years previously, had already inflicted upon a defenseless chemical public, a thirty-four page article in the Annales de Chimie et de Physique (T. VII, pp. 499-532; 1886) in which he had presented his first and only exact values of the atomic weights resulting from the self-same analyses of Stas. Neither before, nor after these diverse and sundry occasions, has the said Van der Plaats made any attempt at determining by the "science of the Laboratory," the falseness or accuracy of any of the data of Stas; it is exclusively in the character of practicing "the art of grouping figures" that this Van der Plaats is before the chemical public, and makes the startling and novel declaration "that the

hypothesis (of Prout) can have nothing in common with the principles and progress of chemistry; it cannot even be made the basis of speculations on the unity of matter," (l. c., p. 1367).

What has just been said is probably sufficient to characterize this particular recalculator of Stas. He has now presented three distinct sets of values which, together with the equal number furnished by Stas himself, gives us poor chemists half a dozen distinct sets of values, to which must be added the several sets calculated by Professor Clarke, and the wonderfully precise set of values for which modern chemical science stands indebted to Professor Ostwald of the University of Leipzig. Quite recently, science has been blessed with a still more accurate set of atomic weights, by Professor Thomsen, of the University of Copenhagen. I think we have fully a dozen sets of values of the accurate and only true atomic weights of the elements determined from the analytical experiments made by Stas some thirty years ago with "a degree of precision that forever places the atomic weights beyond all possible doubt."

And here comes Van der Plaats, the empiric calculator and juggler with figures and with truth, to declare, that the determination of the atomic weights—chemistry of precision—is a matter of the laboratory *exclusively*.* Why did he then "group the figures" from the laboratory of Stas lo! these many times, and fill the chemical world with the noise of his precise and accurate calculations?

I will try to answer this conundrum for him. Stas *was* a great man, *a great analytical chemist*†—but not a true scientist

* Hence astronomy is a science of the observatory, and consequently, Laplace was not an astronomer, and his Mécanique Céleste is no longer a masterpiece of astronomical science. When that imbecil empirical phrase of V. d. P. crept into the Comptes Rendus, the shades of Laplace and Lavoisier must have been temporarily absent from the Palais de l'Institut.

† As such I recognized him when joining the Manifestation, (p. 70). Besides I withheld my critical papers from publication for over a year, so that no shadow might darken the festal day of the great analyst.

in the broad acceptance of the term. Now this excellent analyst did make most careful and accurate determinations, and I venture to say that, under the same conditions, with the same amounts, the best chemist will obtain practically the same results exactly, as those obtained by Stas. But as Schiller has remarked:

> Wie doch ein einziger Reicher so viele Bettler in Nahrung
> Setzt! Wenn die Könige bauen, haben die Kärrner zu thun.

The king-analyst Stas did put up a great big building, and a good many just such men as Van der Plaats, have kept themselves busy for over a dozen years with the recalculations of the results of this King-Analyst, without ever reaching down to the foundation of that building. But while the others, modestly, have been satisfied with furnishing a single set each, of true and exact atomic weights, Van der Plaats has already produced three such, and will probably furnish many more.

Since Van der Plaats is in the habit of *arbitrarily excluding* such of Stas' "laboratory-science" as he deems advisable (l. c., p. 518, p. 512, p. 522, etc.), there is no limit to the number of different systems of exact-and-only-true atomic weights that he will be able to produce—say a new set of values with every new Spring. The very thought of receiving a brand new and only true set of atomic weights every new spring, precisely as Schiller's "Mädchen schön und wunderbar" appeared "sobald die ersten Lerchen schwirrten" produces the following, as a preliminary warble of thanks to Van der Plaats—which tribute, by a judicious application of the method of the least squares, could no doubt, be greatly improved in roundness:

> He brought us new atomic weightjes,
> That ripened lately in his mind—
> Of Stas he dropped some other deeltjes,
> And so, another set did find.

HANS PETER JÜRGEN JULIUS THOMSEN.

The eminent Professor of Chemistry of Copenhagen* has seen Van der Plaats recalculation and, naturally, has come to the conclusion that the results of Van der Plaats neither agree with one another, nor with the analyses of Stas.—See Zeitschr. physik. Chemie, XIII, p. 726; 1894.

Prof. Thomsen proceeds forthwith to furnish us another set of values representing the analytical data of Stas much more accurately; and how excellently he has succeeded, he shows in a table of six-place figures, on page 734. Thomsen just mentions that he has omitted certain of Stas' determinations; these happen to be amongst the most famous of all the analyses of Stas, namely the "complete syntheses of the silver iodide."

He also judiciously drops the dissociation of potassium chlorate and only uses the results obtained in the wet way. It will be remembered how Ostwald took both of these conflicting analyses and desperately calculated that wondrously small probable error we did dwell upon for a few moments (supra, p. 42).

Really, it is not necessary to follow modern chemical science further, as it is exhibited in these special treatises, and in the constantly thickening volumes of our chemical annals.

When in connection with the German exhibit at Philadelphia in 1876, Commissioner *Reuleux* declared the motto of German Industry to be "billig und schlecht," his countrymen abused him, but profited by his judgment — and their grand exhibit at Chicago last year was the result! May I hope that my

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* Professor Thomsen was a student at the Polytechnic School of Copenhagen a few years before I entered the same. Personally we never met.

It is exceedingly distasteful to me to be obliged to examine his recent Stasian contribution, which is as unfortunate as his earlier work on the constitution of benzol and the aromatic compounds, (Oversigt, Kjöbenhavn, 1885. p. 131).

But every reader will understand that these matters represent mere side-issues to Professor Thomsen; the great work of his life has been the systematic investigation of the caloric phenomena of chemical processes. In that field, his labors have placed his name in the front rank of modern investigators.

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drastic, but truthful, representation of the disgraceful condition of the highest branch of chemistry, will lead to equally happy results? I expect, of course, to be covered all over with abuse; but I hope, that the younger chemists will investigate the question raised for themselves.

In conclusion, I will try to explain how Thomsen seems to have come alongside of a Van der Plaats. Thomsen has made a curious new set of determinations of the atomic weight of Hydrogen, and found it almost exactly equal to unity, on the scale of O=16. See Zeitschr. physik. Chem. XIII, p. 405; 1894.

In his reductions he used the Stasian values for chlorine and nitrogen. But it is one of the best established results of the school of Stas, that for O=16, hydrogen is considerably in excess of unity, varying from 2 to 9 thousandths, that is, practically *one per centum*, according to the different determinations.

A thorough man, like Thomsen, necessarily saw that his analysis involved a sort of reductio ad absurdum of the whole system of Stasian atomic weights. He necessarily would look for an explanation of the conflicting values. He took the "latest out," that is the last sets of atomic weights of Van der Plaats (1893). He found that they did not agree amongst themselves, nor with the data of Stas; Thomsen states so in his paper (l. c., p. 726).

His next step was a necessity. He tried to recalculate the analyses of Stas for himself. He used his own judgment in throwing out analyses — precisely as Van der Plaats has done these many years, and as they frequently do in American Ward Meetings, and precisely as they are reported to have done in long past centuries, when the Homousians and the Homoiusians wrestled about their momentous distinctions. Thomsen obtained exactly what he came out to get in that richly worked store-house, by using the proper *method of exclusions*. As final result he obtains

$$H=0.9992$$

which pleases him, being 0.0003 larger than what he obtained before, and therefore, that much nearer the unity he justly thinks it ought to be. (Continued on page 62.)

RESULTS OBTAINED BY RECALCULATION OF THE ANALYSES OF STAS.

Authority.		Ag	Cl	S	N	H	Pb
Stas,	1860	107.943	35.46	32.0742	14.041	.....	206.92
"	1865	.930	.457	.0742	.044	.....	.92
"	1882	.930	.457	.0742	.055	.....	.92
Van der Plaats,	1886	.930	.456	.06	.05	1.007	.91
"	1893, a	.9244	.4565	.0590	.0519	1.0055	.9308
"	1893, b	.9202	.4515	.0576	.0421	1.0085	.9089
Thomsen,	1894	.9299	.4494	.0606	.0396	0.9992	.9042
Clarke,	1882	.923	.451	.058	(.0291)	1.0025	(207.079)
Ostwald,	1891	.9376	.4529	.0626	.0410	1.0032	.911
"	probable error	.0037	.0037	.0042	.0037	.....	.009

The Clarke values in brackets are not from Stas' determinations exclusively, and have only been added for comparison.

On the face of it, the ordinary chemical reader will be impressed by papers, such as those of Van der Plaats and Thomsen, as something very profound and scrupulously exact; *profound*, because he does not understand the muddle any more than Thomsen and Van der Plaats do themselves; *exact*, because they are constantly debating about minute differences, utterly insignificant, while leaving the broad question untouched — in fact, they have denied that there *is* a broad and deep question of principle.

We shall hurry on to the consideration of this very question, which though declared dead is worrying them badly. We must, however, first present a synopsis of the principal values obtained, and also briefly look into a couple of additional special books on the atomic weights. (See Table page preceding.)

GEORGE F. BECKER.

In 1880, the Smithsonian Institution published this author's Atomic Weight Determinations; A digest of the investigations published since 1814.

This valuable book* of 150 pages gives a very complete reference to the original publications and final data of the atomic weight determinations made during the sixty years from 1814 to the middle of the seventies. It is one of the last publications in which the O=100 of Berzelius is used, in connection, however, with the present O=16.

* ATOMIC WEIGHT DETERMINATIONS: A Digest of the Investigations published since 1814. By George F. Becker. Washington: Smithsonian Institution August, 1880; pp. 149, 8vo.

Lothar Meyer and Karl Seubert.

This book* is the most pretentious of all the recalculations, as might be expected, since Lothar Meyer is the real "*author*," and Karl Seubert the man who has done the actual drudgery—as is very plainly seen in the preface by Lothar.

No other work is so absolutely destitute of a scientific basis. The atomic weight of hydrogen, which is notoriously uncertain to fully one per cent., has been made the standard; consequently, all the atomic weights given are fluctuating to the extent of one per cent.—amounting to a full unit for silver, and two full units for lead.

There is no reason for this, except the notion of Lothar Meyer, that the atomic weights of the elements ought not to be exact multiples of any number.

No real data of weighings are given; for the total *sum* of all weighings, and the number of determinations made, as well as the greatest and least ratios, are not weighings. Hence the book is of no use to the special student on this subject.

The numerical data given are not reliable. Thus, Louyet's determinations of Calcium Sulphate from Calcium Fluoride are given (p. 184) at

Mean	1.7353	Min	1.735	Max	1.736
Instead of	1.7435	"	1.745	"	1.746

an error which is not merely typographical, for it produced an

* Die Atomgewichte der Elemente, aus den Originalzahlen neu berechnet von Dr. Lothar Meyer und Dr. Karl Seubert. Leipzig: Breitkopf & Härtel, 1883; pp. X, 246, 8vo.

enormous effect on the atomic weight calculated by Meyer and Seubert, namely 19.15 for O=15.96 or 19.19 for 16.00; instead of 19.00, which results from Louyet's determinations, and also is the true value.

No doubt, Lothar Meyer dislikes the "incorrect" round numbers (preface p. V). We shall pay our best compliments to this most peculiar "famous" chemist of Germany, when we come to the consideration of his "discovery" of the "periodic law."

While all the numerical results, and some of the reputed data of observation, contained in this book, are useless, it may serve the purposes of an *index* to the papers on atomic weight determinations for the period covered; but is fit for nothing else.

Being the most absurd of all the works published on this subject, it had naturally a wonderful influence in these modern days, especially in Germany. The Berlin "Chemiker Kalender," until about a year ago, gave the atomic weights according to this peculiar standard, and nearly all analyses in Germany were "calculated" according to these false atomic weights; in other words, the analyses were, of necessity, falsified.

The influence of these tables has extended even to this country, for the new United States Pharmacopœia has adopted these spurious and false atomic weights throughout.

It is the old story over again. The bigger the humbug, the better and the quicker it takes. But the atomic weights of the chemical elements should not be subject to such influences. The fact that they have been so influenced shows to what extent this most important branch of chemical science of the last quarter of a century has been degraded for the lack of sound criticism. It is indeed time that this deplorable condition cease.

Vox Clamantis in Deserto.

Exactly a quarter of a century ago, I read a paper "On the Classification and the Atomic Weights of the so-called Chemical Elements, with Reference to Stas' Determinations," before Section A of the American Association for the Advancement of Science at its meeting at Salem, Massachusetts, August 18—24, 1869. This paper is published* in full pp. 112—124 of the Proceedings (Cambridge, 1870) of that meeting.

In those early days, the American Association had not yet divided itself into numerous small sections, in imitation of the much larger British Association; only two sections existed, namely one for the physical (A) and another for the natural (B) sciences.

With the "progress" of science in America, the increasing number of "specialists" that have no broad scientific education, but like factory hands, can turn some few buttons, the Association has greatly lost in scientific importance.

But even in that day, the crowded audience contained very few who seemed to understand, and only one who fully comprehended, the main point made by me, by declaring after a brief discussion, that my point of comparison with Kepler's Laws, was "well taken." That man was none less than Professor Benjamin Peirce of Harvard University.

But with that exception, and especially as far as the Chemists

* Also as No. 4 of my Contributions to Molecular Science.

of the audience were concerned, my voice was that of one crying in the wilderness.

I think it of sufficient importance, however, to insert here the entire third (and last) section of that paper, from the proceedings, in order to show that even so far back as 1869, I had *demonstrated* the existence of a systematic error in the result of Stas. It throws a strong light on the condition of chemical science, that this positive clue to the errors in the *results* of Stas, has not been recognized and much less developed by any chemical worker or calculator during the quarter century that has elapsed since the clue was placed in their hands.

The following is the Section of my paper referred to, in which the pages of the original publication are marked in brackets.

"III. STAS' DETERMINATIONS.

[122] "Very much is said about these very interesting determinations of the atomic weight; but we believe that the true importance of these great labors is hardly estimated yet. Most chemists seem to think that the chief importance of the painstaking work of STAS is to disprove and forever reject the so-called hypothesis of PROUT; and with the destruction of this hypothesis they seem to think that all the palpable harmonies of the atomic weights, and particularly all relating to "*pantogen*" is annihilated. We are inclined to think that just such careful determinations *will demonstrate* the correctness of a law of a common divisor (equal one-half the atomic weight of hydrogen?) for all elements, and prove some essential features of the *structure* of the element atoms.

"In order to approach this subject let us grant all that STAS does claim for his figures; that is, they are exact to the first or even the second decimals. *Let us see, what these figures, if they are so accurate as claimed, really do prove!*

"The values of STAS are actually obtained for oxygen equal to 16. Let us represent these values by S. The atomic weights in accordance with PROUT'S LAW (referred to one-half hydrogen) we shall for the sake of convenience call the *normal* atomic weights, A. The deviation of observation from these normal values we denote by D,

$$D = S - A \text{ or } S = A + D.$$

The deviation per unit of weight will then be

$$d = \frac{D}{A}$$

"The values A, S, D and d are given in the following table, [123] S being taken from *Fresenius'* *Zeitschrift für Analytische Chemie*, 1868, p. 169.

	A.	S.	D.	d.
KALOIDS, *Ka*, mean				+0.00284
Lithion, Li	7	7.022	+0.022	+0.00314
Sodium, Na	23	23.043	+0.043	+0.00187
Potassium, Ka	39	39.137	+0.137	+0.00351
PHOSPHOIDS, *Φ*				
Nitrogen, N	14	14.044	+0.044	+0.00314
PANTOIDS, *Γ*				
Hydrogen, H	1	1.002	+0.002	+0.00200
SULPHOIDS, *θ*				
Oxygen, O	16	16.000	±0.000	
CHLOROIDS, *X*, mean				—0.0008
Chlorine, Cl	35.5	35.475	—0.025	—0.0007
Bromine, Br	80	79.952	—0.048	—0.00060
Iodine, Io	127	126.850	—0.150	—0.00118
CUPROIDS, *Kυ*				
Silver, Ag	108	107.930	—0.070	—0.00064

"It is apparent that d is nearly constant for the same genus, and very nearly +0.003 for the Kaloids, —0.001 for the Cloroids. In other words the deviation—whatever be its cause—is nearly proportional to the absolute weight determined!

"Another very peculiar fact is the *positive* sign of the deviations, D and d, for the elements which are electro-positive in regard to the standard (oxygen), while the deviations are *negative* for the elements which are electro-negative in regard to oxygen. Silver forms the only exception to this rule. At the same time its deviation d is only 0.0006, or much *less* than that of all other elements except bromine; and the electro-chemical difference between silver and oxygen is not considerable either.

"We conclude, therefore, that STAS' determinations S of the atomic weights deviate from the normal atomic weights A by small quantities D which

[124] "*First*, in regard to sign agree with the electro-chemical sign of the element in regard to oxygen (silver excepted); and

"*Second*, are nearly proportional to the atomic weight itself.

"Granted the accuracy of the determinations of STAS, the conclusions just given follow. We accordingly have a case in chemistry like that which astronomy would have offered if the perfection of the instruments and methods of observation had progressed more rapidly than theory, after the propounding of KEPLER'S laws. Then deviations from the elliptical orbits would have been observed, and it would have been discovered that these deviations were closely related to the relative position of the planets. If an expert observer on account of these deviations should have rejected KEPLER'S laws as disproved, he would have been greatly in error, because, as we now know, the observed deviations are consequences of the same law of gravitation on which KEPLER'S laws depend.

"Now, theoretical chemistry is vastly behind practical (empirical) chemistry, in fact, so much behind this latter that the claims of mathematical chemistry are generally either ignored or derided. We shall, therefore, not venture to give our explanation of the deviations d; we probably only would deter from those much needed researches, which will demonstrate what we now must leave as merely probable."

CHAPTER III.

CRITICAL EXAMINATION

OF THE

DETERMINATIONS OF STAS.

The mere presentation of the conflicting results obtained by the recalculators of Stas has sufficed to show that not one of the atomic weights, claimed to have been determined by Stas with such wonderful precision, is really known to a certainty, and that, on the contrary, the atomic weights of all elements appear to be mixed up in inextricable confusion.

But the amount of analytical work done by Stas is too great to be left unproductive to science. Let us endeavor to examine it without preconceived notions of any kind, simply and directly from the standpoint of a chemist. We do not need to create a reputation as a mathematician for ourselves, and the mere application of the handicraft involved in the method of the least square, could not possibly give such a reputation outside of the circle of chemical analysts.

But as I desire the especial attention of exactly this class of scientists, I will refer them to an experience which must be common to all, and which will give them the clue to the mistake made by our chemical calculators, Ostwald, Clarke, and the others—including even Stas himself as the first calculator of his own analyses.

We all know how strong a hold the systematic course of chemical analysis takes on the younger chemist; how he will apply it and work for hours, where the chemist of experience, by a few simple, preliminary tests, in a minute, ascertains the general chemical nature of the substance in question. Of course, this mistake may also be made by others than beginners. Thus the elaborate analysis of the Orgueil meteorite by Pisani* does not indicate the presence of sulphates; but putting a few grains of this meteorite in a drop of water, the cement is dissolved, and in a few minutes beautiful crystals—even twins—of gypsum appear in the marginal portions of the drop examined under the magnifier or the microscope—as I had occasion to recognize recently.

Now, the Revisors and Recalculators of Stas are mathematically in the condition of the young student of chemical analysis, who brings the entire formulary of the general analytical course to bear in each simple case, because the principles of analysis have not yet been assimilated by him and become part of his being. Hence the foremost Recalculators employ a formal mechanism of calculation instead of attacking the problem in a broad mathematical spirit.

Let us now undertake a plain, matter of fact, chemical examination of the analyses of Stas, with a view of a critical determination of the positive, scientific results obtainable from his extended and laborious analyses.

To attain this object it will not do for us to follow the example of Stas and his calculators in the blind adoption of wild hypotheses; we must strictly confine ourselves to matters of scientific fact, and not let "purely mental conceptions" ensnare us away from "experiment, measure and calculation," (see address of Academy of Amsterdam, p. 36.)

For example, I hold that it is impossible to know the exact

* Meunier, Géologie comparée. Paris, 1874; p. 141.

weight of a substance, except it be ascertained by actual careful weighing on a good balance; this furthermore presupposes, that the substance itself is in a weighable form, a constant and fixed chemical and physical condition.

But Stas has not conformed to this rigid rule of science. He has labored long and with extreme skill in producing what may be properly called an analytical consommé; he has assumed to know exactly what compound this soup contained, and guessed at the weight of substances in the same. Upon such, purely mental conceptions he has built his atomic weights, and so have all his recalculators done after him.

When we come to such a condition of things in the work of Stas, we shall, in detail, prove that the above description is exactly true—and shall leave such spurious determinations to students of metaphysics and to friends of the culinary art.

Of substances that can be produced in chemically pure state and in a weighable, physically and chemically reasonably permanent condition, several of the metals are good examples. Stas has produced admirably pure silver and excellently pure lead. We may safely take these metals of his, when carefully weighed by this master of analysis, as representing definite chemical entities in a definite amount, expressed with precision by the weight* given by Stas himself.

This will be our *first rule*, to which I trust there will be raised no objection. While it is true, that even the distilled silver is not absolutely chemically pure, we will accept it as pure within the limits of our experience.

* Ostwald wants *mass* to take the place of the weight, varying with place of weighing, (Lehrbuch I, p. 2). But the weights vary exactly in the same proportion. The actual determination of mass involves the determination of the acceleration of gravity; hence is very crude as compared to the operation of weighing. Chemists will continue to weigh and use weights.

SECTION I.—SYNTHESIS OF TERNARIES.

One of the most famous series of experiments of Stas is the conversion of a definite amount of such a metal into its nitrate and sulphate and the determination of the weight of these salts so obtained. Now such chemical conversion, without loss or gain of the amount of metal used, is a most difficult operation; the conversion should be complete, and the product should contain nothing else whatsoever but the compound intended. Finally, these compounds must be in a weighable form, that is physically and chemically sufficiently constant under our ordinary conditions.

All chemists will agree on these conditions, which it is, however, infinitely more difficult to fulfill, than the obtaining of the definite amount of the metal started with. Hence the weight of the *metal is the independent variable* and the weight of the compound must be considered the *dependent variable.*

Also here we may cheerfully admit the impossibility of absolute compliance with all of these conditions; at the same time we ought to grant that *methods* and *men* come in to their fullest weight, and will, individually, approach the fulfilment of these conditions to a greater or less extent.

As to *methods*, we all understand some of the essential conditions: no transfers from first vessel used, no turbulent action at any time, etc., etc. Our special treatises are full of these matters, and only serious infractions of these rules would deserve mention here.

As to *men*, we shall join the school of Stas in all they wish to say as to his skill as an analyst. But we will not admit, that he is the only expert analyst, and that whenever the results of any other chemist differ from those of Stas, that always Stas was right and the other chemist wrong. This common opinion of the

school of Stas is one of the fixed mental conceptions which have taken possession of them, and is in glaring conflict with the plainest results of "experiment, measure and calculation," as we shall show at the proper time.

We shall find, as the result of the most careful and critical examination of the data obtained by Stas and by Dumas, that the oft accentuated *conflict* is also one of the manifestations of the exuberant imaginations of Stas and his school; for the determinations of Stas confirm those of Dumas, when examined as all scientific data should be examined: by a cool, critical comparison of *all* the facts in the case.

On the question of the nature of the product, loss or gain of that product, there might be no end of questionings. But our object being simply a straightforward, scientific examination of the results obtained by Stas, we will *as Rule II*, grant the friends of Stas all that they possibly could ask, by accepting the final weights obtained by Stas as the weights of the product he considers it to be and obtained from the metal he has taken. We furthermore will carefully note all special remarks made by Stas himself, about the process and the results, and also accept these statements as final. We must, however, reserve the right to show up larger errors in detail, wherever they may occur.

Under these conditions, we expect the entire school of Stas, that is, all chemists, to join in this critical examination.

To simplify and shorten our work, let the *metal* taken have a weight q, the *salt* (nitrate, sulphate) formed therefrom have a weight p; then the *amount of salt per unit of weight of metal* evidently is obtained by dividing the weight of the salt found by the weight of the metal used. That is:

$$a = \frac{p}{q}$$

This ratio is the direct expression of the chemical operations made; we shall call it the *analytical ratio*. It involves no

theory, no supposition whatsoever, beyond that of the uniformity of the product obtained. It is the simplest, most direct expression of the analysis made, granting all that is claimed by his school: pure, definite metal and compound, no loss, no gain, as stated above. Moreover, the school of Stas is using this ratio, referring to 100 of the metal as the unit. This plain, matter of fact examination of the determinations of Stas, we shall now proceed to make, beginning with the most admired of all, the synthesis of *silver nitrate.*

A. SYNTHESIS OF SILVER NITRATE.

STAS syntheses of silver nitrate, from purest silver and nitric acid, are the most famous of all quantitative determinations on record. Stas himself was particularly proud of this work of his, since he twice—both in 1860 and in 1882—specified these determinations in his challenge to the chemists of the world. His first two publications were each marked by a series of such syntheses,* in which he used from 77 to 405 grammes of silver in each. They were all carried out with extreme care. The determination No. 7, in which it was impossible for him to collect, separately, the minute amount of silver nitrate that might have been carried over, is by his calculators generally thrown out; we shall, accordingly, do the same. The second series comprises only two determinations, but as some question had been raised by Marignac concerning the first series, Stas was doubly careful in this last series. The amount of silver used averaged one hundred grammes only—less than one fourth the amount he had used in No. 6.

The data of these determinations are given by Stas (Edition Aronstein, p. 305 and 315). Sebelien also gives full data, but

* The first series published in 1860, comprised 8 separate determinations.

Clarke gives none of the weighings, so that on this important point his book is of little value. Van der Plaats (p. 518-519) gives and uses the second series only—that is, he used two of the ten determinations made by Stas, throwing away the other eight. We shall see how great an influence this omission of the first series has on the resulting values given by this author falsely as the expression of Stas' determinations.

In each determination, Stas presents two distinct values for the weight of the silver nitrate obtained; in other words, he applies the term silver nitrate to two different bodies.

First, *dried* he calls silver nitrate, when it has, under the conditions of his experiments, attained a constant weight at about the temperature of beginning fusion. After having determined this weight, he fuses the nitrate completely at but a slightly increased temperature, to avoid its decomposition, and now determines its weight again as *fused nitrate.*

The following table gives all of the determinations, carefully revised by comparing the different authorities which, however, happily show no difference whatever in these figures.

[TABLE 4.]

SYNTHESIS OF SILVER NITRATE, BY STAS.

ABSOLUTE WEIGHT IN GRAMMES.

No. of Determ.	Silver taken.	Silver Nitrate obtained. Dried.	Fused.
1	77.2684	121.6919	121.6749
2	99.9925	157.5025	157.4770
3	199.986	314.969	314.933
4	299.996	472.4303	472.403
5	300.000	472.432	472.411
6	404.997	637.755	637.713
7	200.000	314.921	314.901
8	200.000	314.977	314.938
9	136.2952	214.6600	214.6462
10	82.3231	129.6555	129.6420

These are the data of observation, as published by Stas. We accept them as such, and subject them to the only legitimate process of calculation, by dividing the weight of the silver used into the weight of the nitrate obtained, so as to ascertain the amount of silver nitrate obtained per unit of weight of silver taken. This we have called the analytical ratio.

Table 5, gives the results of this calculation. In this table, the weight of silver used is only stated to the decigram, as it serves here merely the purpose of reference.

[TABLE 5.]

SYNTHESIS OF SILVER NITRATE. STAS.

No.	Silver. (to dgr.)	Analytical Ratio. Dried Nitrate.		Fused Nitrate.	
1	77.3	1.574	92	1.574	74
2	100.0		10*		81
3	100.0		85		77
4	300.0		76		71
5	300.0		78		70
6	405.0		71		63
7	200.0		60		50
8	200.0		88		69
Mean (omitting 7)			85.7		72
9	136.3		96.3		86.2
10	82.3		95.9		79.5
Mean,			96.1		82.8

* Third place is 5, instead of 4.

As to the numerical data here given, I will observe that the ratios for the first series (Nos. 1 — 8) are those given in Aronstein, and also by Clarke. Sebelien gives a different value for Nos. 7 and 8 in the fused salt; but his value I find in conflict with the weights stated in Table 4. The ratio for the dried

Nitrate of the second determination I find smaller by 4 units in the fifth place than the weighings require; but I keep the figure as furnished by Stas, because my value would increase the divergence of the results of Stas, that is, show against him.

For the second series of determinations, Nos. 9 and 10, we find the ratios given by Van der Plaats to agree with the weighings of Table 4; hence it is these we have given. Of course, all ratios have been carefully calculated by me, using seven-place logarithms.

In table 5, we have before us the results of the two most famous series of quantitative determinations which the science of chemistry possesses. The analytical ratio gives the amount of silver nitrate (dried or fused) obtained by Stas from a unit of weight of pure silver, while as a matter of fact he used the amount of silver stated to the nearest decigramme in each line.

These analytical ratios are not new results — they are the identical data used by Stas and his recalculators, or at most differ but slightly therefrom, as specified above.

But here it is where we must part company with all the chemists that have preceded us — for the simple reason that they have not conformed to the principles of science, but have adopted false hypotheses and arrived at a chimera — to use their own language.

Stas himself, and all his recalculators, have looked upon these columns of figures, and noted with pleasure that the first four digits—which we therefore have printed at the head only—are identical, and that the fourth decimal does not vary much either.

They have, accordingly, taken the mean value as marked on our table—omitting the seventh determination for the reasons stated above—and thus found, as the final result, for the amount of silver nitrate obtained from a unit of weight of silver, the following mean values:

First series.		Second series.	
Dried	1.574 857	Dried	1.574 961
Fused	1.574 721	Fused	1.574 828

It will be noticed that these mean results are far from identical; the weight of the fused nitrate is about 14 units in the fifth place (hundred thousandths) less than the dried silver nitrate, though these, if they were determinations of the amount of true silver nitrate obtained from the same unit of weight of pure silver should agree. Furthermore, the means of the second series are about ten units in the fifth place larger than those of the first series; that is, pure silver gave Stas about one sixteen thousandth more of nitrate in 1865 than in 1860. Did silver change in that time? Did the "combining capacity" of silver progress from that flat basis from which Dr. Fittica drove it to secure a wider field for his investigations? (See p. 37.)

It will be granted that by taking either of the four means above stated, there will, of necessity, result four different series of atomic weights for silver and all other elements.

And we should not for a moment suppose, that the differences here brought out are so very insignificant. For example, we shall soon learn, that the influence of any error in this ratio on the atomic weight of nitrogen is multiplied by the atomic weight of silver, 108. Hence the extreme difference of these four means, namely 24 in the fifth place, or 0.00024, amounts to 0.02592 or 0.026 on the atomic weight of nitrogen—a quantity far beyond the extreme possibility according to the calculation of probability by Stas (p. 33).

But the individual ratios vary (omitting 7) from 60 to 110 in the fifth place, or differ by 50 of that unit, that is 0.00050, which will cause a variation of 0.054 in the atomic weight of nitrogen.

Now this amount is fully equal to the largest deviation from the exact 14 found by any of the recalculators, as will be seen by reference to p. 61.

It thus appears, that the actual differences in the observed ratios of silver nitrate, are fully sufficient to account for the departures found for the corresponding atomic weight of nitrogen; in other words, *these departures are correlated and equivalent to these apparently minute differences in the silver nitrate ratios resulting from the "wonderful" syntheses of silver nitrate effected by Stas in* 1860 *and* 1865.

It will not do, therefore, to simply say, that these differences are small, only affecting the fourth place one or two units, and may be neglected. On the contrary, these differences *must* be carefully studied, for on these depend the reality of the departures of the atomic weights from the common values and the unity of matter as well.

Nor will it do, with Van der Plaats, to simply omit the eight determinations of the first series and take only the two determinations of the later series—which involved an amount of silver of only about one hundred grammes, while the first series of Stas involved from 70 to 400 grammes in the different single determinations.

There is plainly something deeper in all this than can be seen by a mere glance of the eye at the "agreeing" figures of the columns of table 5.

Now, what should a scientist do in a case like this? What is the best means at our disposal for examining the relations of quantities, expressed by numbers? Why, we can see them best by looking at them, that is, by representing them to the eye as portions of space, as geometrical quantities.

In table 5, we have two sets of correlated quantities: the amount of silver used, and the ratio of the silver nitrate obtained (dried or fused). The weights of silver we will take as abscissae. The corresponding ratios we will take as ordinates.

To represent the analytical ratios, we will count them from a convenient point on the vertical. Since the formula of silver

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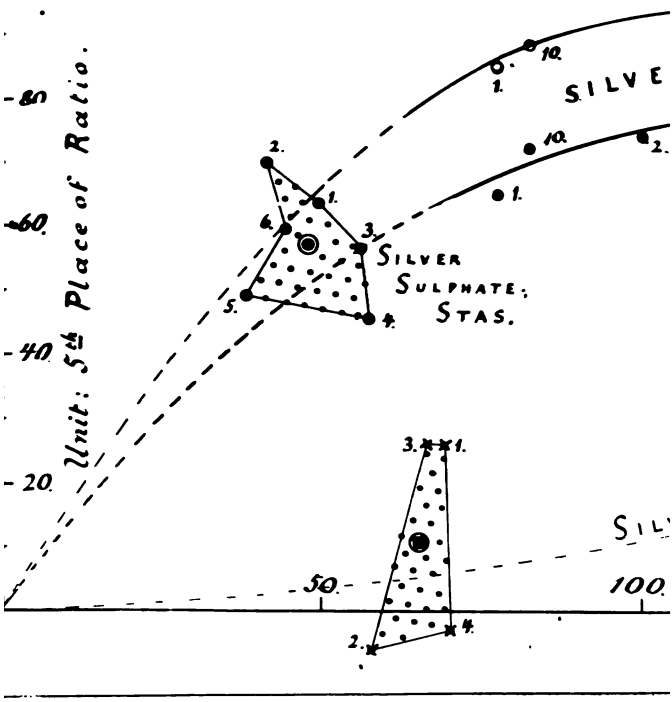
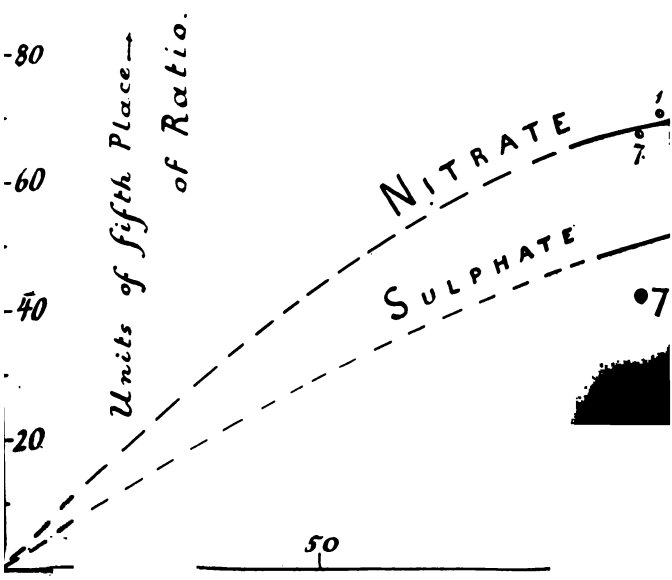
PLATE I.


Unit: 5th Place of Ratio.
80
60
40
20
50
100
SILVE
SILVER
SULPHATE;
STAS.
SIL


Units of fifth Place of Ratio.
80
60
40
20
50
NITRATE
SULPHATE

ıte is AgO_3N, and since for our common atomic weights =108, O=16, N=14), this amounts to 170, the (common) *ıic ratio* is

$$r = \frac{170}{108} = 1.574\ 074$$

:he analytical ratios (Table 5) are seen to *exceed* this atomic ı. Let us calculate the amount of this *analytical excess* for determination and for both the dried and fused nitrate. In ɜ of the *fifth* decimal place, we need only subtract 7 from ınalytical ratio *a* in order to obtain the analytical excess, *a-r*.

ABLE 6.]	SILVER.	SILVER NITRATE.	
Exp. No.	Metal taken.	Analytical Dried.	Excess (5th place) Fused.
1	77.3	85	65
2	100.0	103	74
3	200.0	78	70
4	300.0	69	64
5	300.0	71	63
6	405.0	64	56
7	200.0	53	43
8	200.0	81	62
9	136.3	88.9	78.8
10	82.3	88.5	72.1

ese co-ordinated values of weight of silver used and ana- excess found, are represented by a dot each in Figure 1, per diagram of Plate I). In the original drawing made 0 grammes of silver were represented by one inch, as nd the analytical excess of 10 in the fifth place also by ordinate. In this manner, I was able to accurately weight of silver used to the decigramme, and the ound to the millionth (sixth place)—for these hs of an inch on the scale used. The printed

diagram has been reduced by the photo process to one third the original scale.

It will also be noticed that the dried nitrate is represented by small open circles, while the fused nitrate is marked by filled (black) circles of the same size. The three determinations, Nos. 4, 5, 6, are not represented as they would require a diagram twice as long. We shall, however, not omit these determinations on that account from our consideration.

Now, it is apparent at first sight, that these dots representing the analytical ratio for the dried and fused nitrate, mark the two drawn out curves. The only determination decidedly outside is No. 7, and it will be remembered, that Stas himself has stated, that its value is too low, and why. Furthermore, it is shown by the dotted lines, that these curves produced would reach the point of origin of the drawing.

Accordingly, *the analytical ratio found depends upon the amount of silver used in the experiment.* Towards hundred grammes of silver, the analytical ratio increases; above 150 grammes, it quite markedly decreases again. Table 6 shows that for 400 grammes of silver, the analytical excess comes down to 56, which is but little more than half that for 100 grammes in the case of dried nitrate.

Now right here I notice a most curious error in the actual chemical determinations of Stas, an error that has been overlooked by all his recalculators. Namely, he has largely overstated the value of silver nitrate for the highest weight of silver used by him.

All weights given (Table 4) are absolute, that is, they have been reduced by Stas to a vacuum. By subtracting the stated weight in air from this, we see immediately how large a correction Stas applied for this purpose. By plotting these values, as function of the weight of silver used, I find that the correction made use of by Stas amounts to 21 milligrammes per hectogramme of silver in the First Series. By this rule we obtain the

alculated values given below, which are seen to be practically lentical with those actually used by Stas in the determinations pecified—values which he, of course, obtained by observing hermometer, barometer, hygrometer, etc.—the more instruments, the better!

No.	1	2	3	4	5	7
)bs	16.4	20.5	42	63	63	42
'alc.....	16.2	21	42	63	63	42

In No. 8, he has allowed 30, while my calculation gives 42 ngr.; hence the dot, No. 8, placed according to Stas results, is oo low, and should be higher above No. 3; there was a larger ifference between 3 and 8, than reported by Stas.

The most notable error committed by Stas affects determinaion No. 6, in which 405 grammes of silver were used—the ighest amount employed by Stas or anybody else. He has reuced the nitrate to vacuum by adding 150 milligrammes, vhile my rule, found true in all other cases, allows only 84 milirammes. This error amounts to 80 per cent. on the reduction o vacuum, and it is impossible that such variations can occur in ur own atmosphere; the barometer cannot possibly, at any ime, have run up to 54 inches at Brussels! We must, accordngly, subtract 66 mgr. from the weight given for the nitrates nder No. 6 in Table 4, thereby the corresponding ratio in Table , becomes 1.574 45 and accordingly the analytical excess Table 6) is reduced to 38 in the fifth place instead of the value 6 there given. An error of 66 milligrammes in a final weight of tas, is not insignificant. The excess for the dried nitrate is educed from 64 to 46.

Combining the values to a mean for the equal weights of silver used, we obtain the following results:

No.	Silver. Grammes used.	Analytical excess. Dry Nitrate.	Fused Nitrate.
.	77	85	65
, 3	150	90	72
	200	81	62
, 5	300	70	63.5
	405	46	38

These numbers plainly show the same relation—increase, reaching a maximum for about 100 grammes of silver, followed by a *continued* and very considerable diminution.

The universally admired syntheses of silver nitrate effected by Stas in 1860 and in 1865 give per unit of metal, amounts of silver nitrate—whether dried or fused—which *are not independent of the amount of silver used, but regularly and systematically vary therewith.*

The extent of this variation is enormous, running from about 38 to 100 in the analytical excess. It is fully equivalent to 0.067 on the atomic weight 14 of nitrogen, which Stas and his school derive mainly from these experiments.

But if the analytical ratio varies, forming a parabolic curve over the corresponding weights of silver as abscissæ, it is manifestly *chemically* and *mathematically* impossible to take a *mean* of these ratios; of course, any calculator may determine such a mean, but such a mean can have absolutely no value in science.

This fact, *the systematic and continued variation of the amount of nitrate obtained as function of the silver used*, does entirely away with all the calculations of Stas and all the recalculations of his admirers. This simple but fundamental FACT they all overlooked—and their work was in vain.*

But if there is no mean, there can be no difference from that mean, and consequently, no probable error. The entire mathematical treatment to which Stas and his recalculators have submitted the syntheses of silver nitrate, was absurd, because it was taken for granted—a mere unsupported hypothesis—that the analytical ratios fell regularly about that mean—nearest it most

* It seems almost necessary to accompany chemical works with elementary explanations, for use by German Chemists of the present. Kolbe has for seen such a necessity in 1876.

Thus, Professor G. Krüss of the University of Munich, has not yet learned to distinguish between a scientific fact and a mere statement (Behauptung). See his contribution to the Jahrbuch der Chemie 1893, p. 49.

The "Docenten" of 1876 have evidently become Professors in 1894.

frequently—and were above all, entirely independent of the amount of silver employed.

Why, the essential constancy of the chemical composition of any compound is always presupposed in analysis. To assume that the percentage of silver in silver nitrate will be found different for a hundred than for two hundred grammes or for four hundred grammes thereof, seems absurd. But the syntheses of Stas show, that this apparently absurd condition obtained most indubitably in his famous syntheses of silver nitrate, which contained a less percentage of silver when made from hundred grammes of silver, than when made from a greater or less amount of the same metal.

But Stas and his successors should have avoided making such rash hypotheses when they were considering experiments involving the very foundation of chemistry; they cried out lustily against others, calling them makers of hypotheses and believers in a chimera. It was a clear case of the thief crying out: stop thief.

This is not the place for any attempt at an explanation of these variations of the analytical ratio with the absolute amount operated upon. All that is necessary to do here has been done in the establishment of the FACT.

In conclusion we may revert to the omission by Van der Plaats of the entire first series and the adoption of the second "more exact series" of Stas, (l. c., p. 518). The diagram shows that the second series, Nos. 9 and 10, does not in any way depart from the others in accuracy; but both determinations of *this second series are near the maximum value* obtained, from which towards greater amounts of silver used, the ratio descends enormously. If, therefore, it were proposed to *select* that series of Stas, which, giving the greatest analytical excess for silver nitrate, would of necessity also yield the largest atomic weight for nitrogen, Van der Plaats could have made no better choice

than he actually did. The reason he gave, we have seen to be false in fact, though he may not have known that.

Van der Plaats also declares (l. c., p. 518) that he is incompetent to choose between the fused and dried nitrate as the true representative of the chemical compound which we call silver nitrate. It is evident that the difference is quite material. Recently, Van der Plaats has published a private letter of April 18, 1886, in which Stas declares that the *dried* nitrate is the true nitrate, because by fusion a slight decomposition takes place, which, however, he shows to have corrected by a change of atmosphere. (C. R., T. 116 p. 1363; 1893). Stas also declares that the ratio is 1.57495 to 1.57497 only for this dried nitrate; but in this, he refers to his second series, exclusively, that is, he gives the one value corresponding to 100 grammes of silver used, and would like to have us ignore his entire first series, which in no way is contradicted by his second series at the point in question. If either is bad, both are equally bad.

It is no longer Stas over Dumas, or Marignac, or any other analyst—it is Stas at one time over Stas at another time; and they seem to be determined to take, as accredited, only those of the values of the regular function established by such of his experiments as deviate the most from the base line corresponding to the common atomic weights. Was this *choice* really altogether unconscious, both in Stas and in his disciple Van der Plaats?

Here we find the school of Stas reduced to the necessity of determining the analytical data by mere choice—data from which the atomic weights are to be calculated. The strangest feature of all is, that their preferences are exclusively for those determinations only, which lead to atomic weights differing the most from the common values of exact multiples. From an exact science, empirical in its nature, and resting on the results of experimental data, even the master of this school has turned to a deliberate selection of data favorable to their assumed hypothesis!

The only legitimate conclusion that Stas and his school of empirics could draw from the data of their own experiments, represented in Plate I, would be this: Chemical compounds do not contain the elements in fixed proportions; for the amount of silver nitrate from a given unit weight of silver, varies continuously and regularly with the absolute weight of silver employed, which amount is a maximum for about one hundred grammes of silver used, and is constantly larger for the dried nitrate than for the same chemical compound when it has been fused. Accordingly, the act of fusion destroys the fundamental property of weight.

Thus, both Berzelius and Lavoisier are disproved by Stas. This ought to be a matter of greater consequence to the empiric, than the bearing of Stas' determination on the hypothesis of Prout.

But neither Stas himself, nor his school, have dared to draw this, the only legitimate empiric conclusion from the famous syntheses of silver nitrate made by Stas; on the contrary, they take special credit in claiming, that Stas above all others, has demonstrated* by his analyses, that chemical compounds do contain the constituent elements in perfectly fixed proportions!

Having considered the synthesis of silver nitrate by Stas with considerable minuteness, we may be allowed in the future to merely present the main facts and indicate the conclusions which necessarily flow from them. We deem it also advisable to present, at every important point, the determinations of other chemists on the question at issue. We shall begin right here, by the consideration of the syntheses of silver nitrate effected by *Marignac.*

Table 7 gives the details of the experiments of Marignac, as

* Ostwald, l. c., p. 14: "proved exact to a ten-millionth!" "The most perfect demonstration of any law of nature!" What a poetic, imaginative soul Professor Ostwald must have! No wonder, he is adopting all sorts of new theories—and wants to destroy the old fashioned science of Newton and Laplace.

copied by Clarke (p. 42) from Berzelius' Lehrbuch, 5th Ed., Vol. 3, p. 1184, and by Sebelien* (p. 139) without reference to original publication in Bibl. univ. de Genève, t. 46, p. 365,1843, which is mentioned in Meyer-Seubert's index, p. 61. Sebelien states that Marignac maintained the silver nitrate, for some time, one or two degrees above its fusing point, in order to expel the last excess of acid.

[TABLE 7.]

SYNTHESIS OF SILVER NITRATE. MARIGNAC.

Determ. No.	Silver Taken.	Nitrate Found.	Analytical Ratio.		Excess (5th).
1	68.987	108.608	1.574	33	26
2	57.844	91.047		01	— 6
3	66.436	104.592		33	26
4	70.340	110.718		04	— 3
5	200.000	314.894		47	40
Mean 1—4, 65.9		.....		18	11

These determinations have also been represented in Figure 1. It is evident that the first four determinations can properly be combined to a mean, which has been plainly marked on the diagram.

This mean, together with the quite distant determination No. 5, gives a preliminary indication of the curve representing the analytical excess for the conditions under which Marignac effected his syntheses of silver nitrate.

While the determinations are insufficient in number, it will already be noticed here, that notwithstanding the apparent enormous conflict between the results of Stas and of Marignac, our diagram shows that all the curves converge towards the origin of the co-ordinates; so that for *small* weights of silver, both Stas

* The error signalized by Sebelien is a mere typographical one, 66 instead of 68 grammes, as shown by ratio and confirmed by Clarke's copy.

and Marignac would have obtained the same values of silver nitrate, if each had continued to work under the same conditions as before.

But we shall not insist on this point here — our empirics would cry out *extrapolation* though we are not determining any value at all — we simply call attention to the *fact* that the curves drawn do meet at the origin. Stas' *experiments* are represented by the full drawn curves — their continuation is only represented by dots. In corresponding cases of other determinations we shall, however, be able to present data all along such a parabolic curve passing from the origin, or the point determined by the atomic ratio, accepting as atomic weights the common values for O=16, N=14, Ag=108 *exactly*.

But as to extrapolation — has not Stas and his school relied entirely upon extrapolation? Has Stas made any determinations for moderate weights? None at all! Both he and his school have tacitly adopted also this additional, entirely unfounded hypothesis, that what they find true for hundred grammes, is also true for fifty, for twenty, for ten, for one gramme. And yet, a simple glance at our diagram reveals the fact that the data of Stas found above 100 grammes are in absolute conflict with this hypothesis — hence it was an unwarranted and misleading hypothesis to assume the constancy of the ratio below 100 grammes.

B. SYNTHESIS OF LEAD NITRATE.

The synthesis of lead nitrate has been effected by Stas with almost as much precision as that of silver nitrate. He first made six determinations in which he dried the resulting nitrate in a current of air. In his second series he dried the nitrate at 155 degrees in vacuum.

We find the fundamental data (weighings), as published by Aronstein (p. 329), copied by the recalculators (Sebelien, p. 149;

Van der Plaats, p. 522); only Clarke here again fails to give these necessary data. The only question raised is represented by the interrogation mark added by Van der Plaats to the weight of the 5th nitrate; but I fail to see any reason for this, because the reduction to vacuum does not show any misprint in the data of Stas, whose ratio is, however, in conflict with the weighings. The evidence is therefore strongly in favor of assuming an error in Stas' calculation of the ratio, 5; for the concordant weights give the ratio 5 which deviates considerably more than the others. In my tables and in the drawing, I retain both.

The following table (8) gives all the absolute weights of Stas, as well as the analytical ratios calculated therefrom by dividing the weight of the nitrate obtained by the weight of the lead used. We also have added the *analytical excess*, calculated in the manner explained, by means of the atomic ratio determined by the common atomic weights (Pb=207, N=14) for O=16, which gives the common atomic weight of lead nitrate, $Pb\ (O_3N)_2=331$, and, accordingly, the atomic ratio

$$r = \frac{331}{207} = 1.599\ 034$$

The calculations have been carried to the sixth place for the first series, but rounded off to the fifth place for the analytical ratios given in table 8 on page 91.

The analytical excess has been plotted as ordinate to the weight of lead taken as abscissa, exactly as for the silver nitrate. The resulting diagram, Figure 2, (the lower part of Plate 1), shows the same strange result: the weight of lead nitrate obtained per unit weight of lead, varies continuously with the absolute weight of lead used, instead of being approximately constant. Excepting the experiment 5 represented by the two points *a* and *b* which both are equally in doubt, but below the curve, we find only No. 3 markedly above the curve. Evidently, the mean of these two determinations 3 and 5 would fall on or

near the curve drawn, which thus truly represents all the syntheses of lead nitrate made by Stas. To give the determinations with the greatest amounts of lead (Nos. 9, 10) an equal influence, the latter part of the curve ought to have passed a little above point 8 and almost reached point 9. But this has, manifestly, no influence on the general result above stated, namely that the amount of lead nitrate produced per unit of metal is a function of the absolute amount of metal employed, instead of being appreciably constant, and above all independent of the amount of metal used.

The mean values calculated by Stas and his recalculators have, accordingly, no existence as scientific data.

Van der Plaats (l. c. p. 522) gives as mean analytical ratio for

Series I. 1.599 713

Series II. 646

and *adopts* the latter to the exclusion of the former; the difference is 67 in the sixth place, or 6.7 in the fifth place.

(To page 90.) [TABLE 8.]

SYNTHESIS OF LEAD NITRATE. STAS.

No.	Absolute Weight. Lead.	Nitrate.	Analyt. Ratio.		Analyt. Excess (5th).
1	103.000	164.773	1.599	74	70.4
2	140.6887	225.0674		76	72.1
3	110.2672	176.408		86	82.6
4	141.9927	227.1527		75	71.5
5*a*	148.616	237.702(?)		44	40.4
b				68	64.6
6	124.348	198.924		74	70.2
7	100.000	159.970		70	67
8	200.000	319.928		64	61
9	250.000	399.8975		59	56
10	250.000	399.914		65	62

Nevertheless, the simple combining of the determinations for (nearly) equal weights of lead used, plainly shows the systematic variation of the analytical ratio, and of the corresponding excess. The doubtful experiments 3 and 5 are, necessarily omitted.

Nos.	1, 7	6	2, 4	8	9, 10
Weight,	101	124	143	200	250
Excess,	72	74	75	64	62

The maximum is reached between 124 and 143 grammes of lead, say at about 133 grammes.

We have not time to consider specially any of the chemical fine points raised by Stas, such as the presence of one twenty-thousandth of silicon in the lead used for the first series; it is evident from the drawing that the quantitative chemical operations outweigh the influence of such a trace. More serious is the fact, that lead nitrate, in so large amounts, has not yet lost all water at 140 and already begins to decompose at 195.

C.—SYNTHESIS OF LEAD SULPHATE.

Stas changed the lead nitrate obtained, in six instances, into the corresponding sulphate, by treating it, in the original vessel, with an excess of pure sulphuric acid. The results are represented in table 9. The analytical excess is calculated by subtracting the atomic ratio of lead sulphate from the analytical ratio found. Since the common atomic weight of sulphur is 32, lead sulphate, PbO_4S, has the atomic weight 303, and the atomic ratio is

$$r = \frac{303}{207} = 1.463\ 768.$$

The data are taken from Aronstein, p. 333, correcting the typographical error in absolute weight of lead (No. 5), as already done by recent calculators, and producing no change in the analytical ratios.

[TABLE 9.]

SYNTHESIS OF LEAD SULPHATE. STAS.

No.	Absolute Weights. Lead.	Sulphate.	Ratio.	Analytical Excess	(5th).
4	141.9925	207.9388	1.464	44	67
5	148.616	217.6141		27	50
7	100.000	146.419		19	42
8	200.000	292.864		32	55
9	250.000	366.0525		21	44
10	250.000	366.0575		23	46

We have represented the analytical excess in the usual way, in Figure 2, where the full circles mark each one of the determinations of lead snlphate made. Taking the mean of determinations 4 and 5, the curve passes above No. 7, but follows in general, a course below that representing the nitrate. All conclusions drawn before, apply to this case with equal force. The amount of lead sulphate produced per unit of weight of lead is not a constant, but varies systematically with the amount of lead employed.

As before, so also here, the mere inspection of the analytical excess already shows the same fact.

No.	7	4,5	8	9,10
Lead,	100	145	200	250
Excess,	42	58	55	45

Sebelien reports (p. 144) that Berzelius obtained, as a mean of four determinations, the analytical ratio 1.46368, which it will be seen is only 0.000 09 less than the atomic ratio, that is, the analytical excess is —9. But while the mean is almost identical with the theoretical value, the four separate determinations (Sebelien, p. 151—152) of Berzelius naturally, differ notably more than those of Stas.

D.—REDUCTION OF SILVER SULPHATE.

We have no synthesis of silver sulphate, but Stas has effected six reductions thereof by means of hydrogen gas (Aronst. p. 217) at a sufficiently moderate temperature. If the temperature is allowed to rise, the reaction is no longer a simple substitution, yielding pure metallic silver and hydrogen sulphate, but there will result silver sulphide and sulphur dioxide, so that towards the end of the process, sulphuretted hydrogen will pass off. Hence, a loss will be sustained, whenever the odor of hydrogen sulphide is noticed. Stas says he always noticed this odor (l. c., 2 17). The extreme difficulty of preventing this loss will be shown when we shall consider Cooke's reduction of silver sulphide. The data of Stas are copied and reduced in the following table. The atomic ratio used is

$$r = \frac{216}{312} = 0.692\ 31$$

since $Ag_2O_4S=312$ gives $Ag_2=216$.

[TABLE 10.]

REDUCTION OF SILVER SULPHATE TO SILVER. STAS.

No.	Absolute Weight. Sulphate.	Silver.	Ratio.	Analytical Excess (5th).
Series I.				
1	72.137	49.919	0.69200	—31
2	60.251	41.692	197	—34
Ser. II.				
3	81.023	56.071	204	—27
4	83.115	57.523	209	—23
Ser. III.				
5	55.716	38.5595	207	—24
6	63.922	44.2355	202	—29
Mean,			203	—28

It will be noticed, that the analytical excess is negative in every instance, precisely as we expected.

Combining the determinations of each series, made with quantities not greatly differing, we obtain the following table:

Series.	III.	II.	I.
Sulphate,	60	66	80
Excess,	-26	-31	-25

These numbers show the usual course. The negative excess is a maximum for about 66 grammes of sulphate reduced, and diminishes both for less and more of sulphate used.

In order to compare this reaction to the synthesis of silver nitrate, we have calculated the analytical ratio sulphate: metal which has the atomic value

$$r = \frac{312}{216} = 1.444\ 444$$

while the analytical values and corresponding excesses are given below (in units of 5th place)

No.	1	2	3	4	5	6
Ratio,	508	514	500	490	493	503
Excess,	64	70	56	46	49	60

These values have been entered in Figure 1. The mean analytical excess is 57 and corresponds to 48 grammes of silver (ranging from 39 to 57 grammes). This mean is also shown in the center of the six-sided figure representing the six reductions individually.

It will be noticed, that this mean falls exactly in the continuation towards the origin of the band bounded by the lines which mark the dried and fused silver nitrate. It is also readily understood, that the deficiency in the amount of silver actually obtained in the reduction of the sulphate, here must appear as an excess of sulphate for the given fixed amount of silver.

This is the proper place to consider the admirable series of reductions of silver sulphate made by *H. Struve* and reported

by Svanberg to the Swedish Academy in 1849 (Sebelien p. 154. The errors in the four ratios 2, 4, 5, 6, given by Sebelien, have been corrected, and were already noticed by Clarke, p. 30). Since Struve operated upon from 5 to 12 grammes of silver sulphate only, the process could be much more easily controlled, exactly as in the admirable work of Cooke, which we shall soon consider.

[TABLE 11.]

REDUCTION OF SILVER SULPHATE TO SILVER. H. STRUVE, 1849.

No.	Absolute Weight. Sulphate.	Silver.	Ratio.	Analytical (Excess 5th).
1	5.1860	3.5910	0.692 44	+13
2	6.0543	4.1922	43	+12
3	8.6465	5.9858	28	— 3
4	11.6460	8.0608	15	—16
5	9.1090	6.3045	12	—19
6	9.0669	6.2778	·39	+ 8
Mean,			30	— 1

It will be noticed that the analytical excess is as many times negative as it is positive; the mean is only minus *one*. That is

Atomic ratio	0.692 31
Analytical ratio	30
Analytical excess	–1

In other words, the reduction of silver sulphate by hydrogen, effected in 1849 by H. Struve, agrees exactly with the atomic ratio of the process.

Though these values, differing but little in absolute weight of the sulphate taken, and oscillating around the atomic value, permit the taking of the arithmetical mean as shown above, they nevertheless plainly mark a systematic deviation, precisely in the direction in which we understand it to be produced by the chemical difficulties involved. Combining, as we usually do, the weights that are nearly equal, and taking the means, we obtain:

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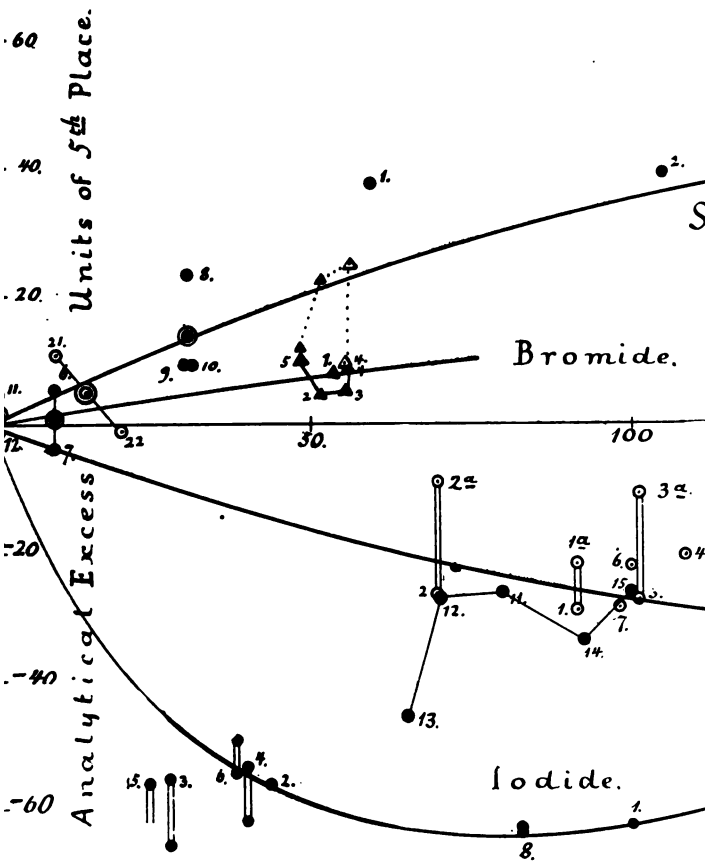
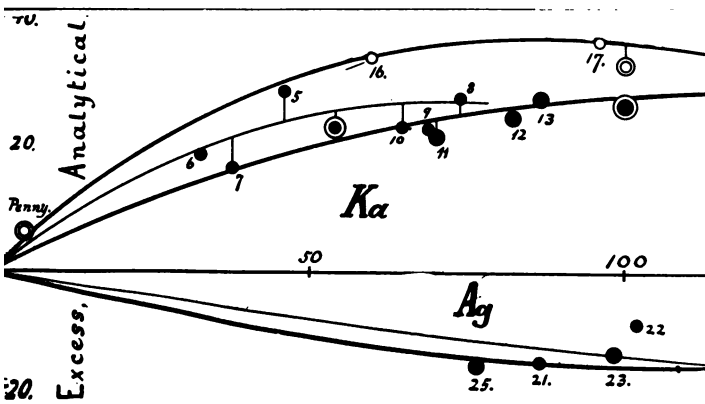
PLATE II.


Units of 5th Place.
Analytical Excess
Bromide.
Iodide.
S
30.
100


Analytical Excess.
Kα
Ag
Penny.
50
100

	1, 2	3, 5, 6	4
t,	5.5	8.9	11.6
s,	12.5	-5	-16
	12.5	-3.4	-16.1

e obtained the calculated analytical excess by sub-
imes the weight of sulphate used from the constant
onstants being determined by the first and last
lose agreement of the calculated and observed value
le weight shows, that on the whole, there is a ten-
ninish the deviation as the weight operated upon
nd that this diminution is nearly proportional to the
d within the narrow limits of this series. The rate of
will, of course, vary with the special conditions under
analyst operates and was much smaller for Stas, than
But the character of the excess — negative — is
arked even for the larger ones of the small quantities
upon by Struve; and consequently the negative excess
ently larger for the great quantities made use of by Stas.
assuredly, this series of Struve should no longer remain
by the corresponding heavier work of Stas, in which
perturbations were considerably greater.
truve's work did give no support to the imaginings of
his School. Hence it was considered of no value.

SECTION II. SYNTHESIS OF BINARIES.

syntheses of binary compounds of silver effected by Stas
rally considered second in importance only to his syn-
f silver nitrate. We have represented all his determina-
binaries in Fig. 3, the upper drawing of Plate II. The
al data are given below, together with the values obtained
as, Marignac and Cooke. We will have to be as brief as
e, without omitting essential points.

A. SYNTHESIS OF SILVER SULPHIDE.

The syntheses of silver sulphide are generally effected by the process first used by Berzelius for obtaining lead sulphide. Stas has varied the process by devising special means for removing a possible excess of sulphur (Aronstein, p. 178); his final product was beautifully crystallized. Table 12 gives all the results obtained. Since S=32, the atomic ratio is

$$r = \frac{248}{216} = 1.148\ 148$$

[TABLE 12.]

SYNTHESIS OF SILVER SULPHIDE.

No.	Absolute Weights. Silver.	Sulphide.	Ratio.	Analytical	Excess (6th).
STAS.					
1	59.4225	68.2482	1.148	525	377
2	105.139	119.6078		540	392
3	191.9094	220.4158		541	393
4*a*	150.000	172.2765		510	362
b		.287		578	430
5*a*	249.076	286.061		489	341
b		.078		556	408
DUMAS.					
6	9.9393	11.4123	1.148	200	52
7	9.962	11.4375		114	−38
8	30.637	35.183		380	232
9	30.936	35.522		240	92
10	30.720	35.274		241	93
COOKE.					
11	abt. 1 gr.	1.1357	1.148	100	−48
12	1.1266	1.2936		233	+85

In the record of the determinations of Stas we find quite a notable discrepancy for Nos. 4 and 5. The first three determinations show that the reductions to vacuum were effected by Stas at the rate of 0.017 milligrammes per gramme of sulphide, very nearly. The following table gives the correction applied by Stas and this value calculated at the rate just stated.

No.	1	2	3	4	5
Stas,	1.2	1.8	3.8	.....	.....
Calc.	1.16	2.03	3.74	1.90	4.86

Now Stas fails to give the apparent weight for Nos. 4 and 5, but instead states the weighing "obtained in vacuo" (Aronstein, p. 179).

No.	4	5
Reduced to vacuum,	172.2765	286.061
Obt. in vacuo,	172.287	286.078
Difference, milligrammes,	10	17
Calc. app. weight,	172.2746	286.056
Excess in vacuo, mgr.	12	22

Applying the calculated correction to vacuum to the reduced weight given by Stas, we obtain the apparent weight above stated; this gives an excess of six times in No. 4 and almost three times in No. 5 of the proper correction. It is indeed strange, that the absolute weight of the silver sulphide formed in experiments Nos. 4 and 5 has been stated by Stas two times, differing by 10 and 17 milligrammes! The calculated apparent weight will not explain matters either, as is plainly evident from the figures shown. This represents an increase of about 70 in the sixth place of the ratio, or seven units in the fifth place, which is from seven to ten times the differences from the mean for the three first determinations, and also ten times the probable error given by Clarke (l. c., p. 29) for the entire series of Stas. It is more than thirty times the value of the probable error of the first three determinations.

684060

It is passing strange that so large a discrepancy in the statements of the weights of the same thing under the same conditions but obtained in two different ways—should exist in the publications of Stas, and have escaped the attention of his numerous recalculators and revising admirers.

In our diagram, the unshaded circles mark this other statement of Stas; both statements *a* and *b* have to be accepted by us as of equal weight, since Stas has, by the omission of the apparent weight, made it impossible for us to prefer either of these two values.

These different expressions of the same fact show in what extraordinary manner the accuracy of the work of Stas has been overrated.

While the values given by Stas as reduced weights, give the five points represented by black dots in our diagram, seemingly close to a straight line, a more careful inspection shows the cu ve plainly marked. The same is also quite evident if we, in the usual manner, combine the determinations made for nearly equal weights.

No.	1, 2, 4	3	5
Mean weight,	100	200	250
Mean excess,	377	393	341

Here the maximum corresponds to the third determination, which exceeds the value for hundred grammes by 16, and that for 250 grammes by 52.

The determinations of Dumas correspond to 10 and 30 grammes of silver, very nearly. We may therefore take the means, namely,

No.	6, 7	8, 9, 10
Weight,	10 gr.	30 gr.
Excess,	45	139

These means have been entered on the diagram, and distinguished by an outer circle. It is evident that the determinations of Dumas most marvellously supplement those of Stas by giving actual determinations for the field in which Stas had to resort to extrapolation. We notice that both the results of Stas and the everyway equally trustworthy data of Dumas, plainly mark the parabolic curve familiar to us from the syntheses of Stas reviewed in the preceding section.

We are even able to record two most important determinations for the low weight of one gramme of silver and the result shows unmistakably, that the parabolic curve of excess over weight passes through the origin.

The determinations were made by Professor J. P. Cooke of Harvard, in 1877. They were not syntheses of silver sulphide, but the reductions of this compound by means of hydrogen gas. He made three series of determinations.

"Highly concordant, and at the same time plainly erroneous, figures were obtained; the error being eventually traced to the fact, that some of the reduced silver, although not heated to its melting point, was actually volatilized and lost." (Clarke, l. c., p. 29).

Cooke accordingly made a second series at a *low redness.* The results are given below:

Silver.	Sulphide.	Ratio.	Excess.
6.5638	7.5411	1.148 89	74
4.3840	5.0364	82	67
2.2470	2.5815	86	71
2.2743	2.6130	92	77
2.2390	2.5724	91	76
Mean, 3.54	.....	88	73

Now this series is remarkably concordant. The differences of the ratio from the mean in the fifth place only 1, 6, 2, 4, 3, giving for the sum of the squares 66, which divided by the pro-

duct 20 of the number 5 of determinations into the next lower number 4, gives 3.3. The square root hereof is 1.83 and $\frac{2}{3}$ thereof, or 1.22, is the probable error.* The unit being the *fifth* place, this probable error of the ratio is 0.000 012 only.

Nevertheless, the mean 1.14888 is much too high, the determinations being still subject to a *constant* error, recognized by Cooke in the temperature being too high. Accordingly he made a new series of determinations at the lowest possible temperature, "below a visible red heat," and obtained the values given in Table 12 under numbers 11 and 12.

These two determinations give, for the mean weight of one gramme of silver, the mean analytical ratio 1.148 166 which is only 0.000 018 in excess of the atomic ratio. That is, the analytical excess is less than two units in the fifth place.

The analytical excess of silver sulphide as function of the weight of pure silver used forms, accordingly, a parabolic curve, passing from the origin (silver and excess both zero) above the axis (excess positive), reaching its greatest heighth of about 40 units of the fifth place for 200 grammes of silver used.

B.—SYNTHESIS OF SILVER CHLORIDE.

Stas made only three genuine syntheses of silver chloride from the elements (Nos. 1-3 in Table 13 below); in the other cases (Nos. 4-7) he prepared the silver chloride in the wet way, by dissolving the silver in nitric acid and precipitating the solution with a volatile chloride, evaporating to dryness and weighing. We have also two actual syntheses by Dumas (Nos. 21, 22), while we have no details concerning the processes used by Marignac (Nos. 11-15). The numerical results are presented in the usual form in Table 13.—For Cl=35.5, the atomic ratio is

$$r = \frac{143.5}{108} = 1.328\ 704$$

* This is all there is to that method of calculation. It is simple enough. Nowhere in this calculation is any agent visible that makes good results out of bad observations or experiments.

[TABLE 13.]

SYNTHESIS OF SILVER CHLORIDE.

No.	Absolute Weights. Silver.	Chloride.	Ratio.	Analytical Excess (6th).	
STAS.				*b*	*a*
I. 1	91.462	121.4993	1.328 413	−291	−220
2	68.8674	92.8145	438	266	90
3	101.519	134.861	431	273	110
II. 4	108.549	144.207	497	207	
5	399.651	530.920	459	245	
6	99.9925	132.8382	482	222	
7	98.3140	130.602	417	287	
MARIGNAC.					
11	79.853	106.080	1.328 441	−263	
12	69.905	92.864	432	272	
13	64.905	86.210	249	455	
14	92.362	122.693	365	339	
15	99.653	132.383	440	264	
DUMAS.					
21	9.954	13.227	1.328 813	+109	
22	19.976	26.542	695	− 9	

The curve, Figure 3, Plate II, represents all data fairly equally well. The mean of Dumas is about 5 units of the fifth place above the axis, and the farthest point (5), determined by Stas with 400 grammes of silver, determines the dotted part of the curve. The determinations of Marignac (black circles) cover the same portion of the curve determined by Stas (open circles), and the deviations are not material.

Within the legitimate precision of the data, the parabolic curve drawn represents all the analyses equally well, whether they were made by Marignac, by Dumas or by Stas. We see that a thorough, unbiased examination, completely removes the invidious distinctions made by Stas and his school; for it is plain that each one determined his portion of the entire curve with approximately the same degree of precision.

The direct syntheses of Stas (Nos. 1, 2, 3) appear twice in the table and on the diagram. Stas first weighed the chloride that had been fused in a current of dry chlorine gas (a); after that he exposed (1) to a current of air and the others (2, 3) to a current of carbon dioxide. The results are distinguished by the letters *a* and *b*. Only values (b) have been accepted by Van der Plaats and others.

It will be recognized at once that the three points (b) are much more "concordant" than the directly determined points (a). Both sets representing the same experiments, how did Stas succeed in harmonizing* the three discordant results?

By turning to the original data (Aronstein, p. 172—173) we see that Stas accomplished this remarkable feat in the simplest manner possible. Since the two points 2a and 3a are concordant, he subjected the determinations 2 and 3 to the same treatment exactly; he displaced the chlorine atmosphere by a current of dry carbonic acid, which removed, on the average, 0.128 milligrammes per gramme of the chloride fused in chlorine. But the lower value (1a) he diminishes by less than half that amount, namely, by 0.053 mgr. per gramme only — that being the loss sustained in a current of air.

This rather startling revelation is nothing but the direct expression of the following weights of the fused silver chloride given by Stas himself (Aronstein, p. 173):

*The probable error of the directly observed values *a* is 27 in the sixth place; for the "corrected" values *b* the probable error is only 5.

No.	1	2	3
In Chlorine,	121.5058	92.8273	134.877
In other gas,	121.4993	92.8145	134.861
Loss, milligrammes,	6.5	12.8	16.
Loss, per gramme,	0.053	0.138	0.118

I confess, I was quite surprised that the many able men, who have critically recalculated the determinations of Stas, and declared in most emphatic language their admiration for the marvellous accuracy of Stas, have left so useful and simple a method without special recognition.

This process really is most admirable. I will therefore try to present it in simple language for general consideration.

If, in a series of determinations, the results are discordant, consisting of several groups of conflicting values, the most admirable concordance will be readily established, by suitably selecting such methods of chemical or physical correction, that the smaller values are made to lose less, while the greater values are subjected to a correspondingly greater loss. The final *corrected* (!) results, will present a fine appearance in numerical column, and yield exceedingly minute probable errors by the method of the least squares, while in graphical representation, the points determined will arrange themselves in an almost straight line, parallel to the line of weights taken as abscissae.

As such methods, actually used by Stas, we have here the suitable change of gas in which the chloride is fused; it will be remembered that in the case of 405 grammes of silver, converted into nitrate, he selected a proper barometer reading in his reduction to vacuum, something like 54 inches; while in the synthesis of silver sulphide, he gave two different absolute weights for the identical portion of sulphide (Nos. 4 and 5).

It is really too bad that Professors Ostwald and Van der Plaats have failed to notice these methods which have contributed to the marvellous concordance which they admire in the results obtained by Stas.

C.—SYNTHESIS OF SILVER BROMIDE.

We have five syntheses of silver bromide by Stas, and by Marignac. The last four of Stas were *complete* synt The results corresponding to the *sum* of the constituents are represented in the table under the letter B, and in the gram by the open triangles. It is generally admitted that "complete" syntheses have no special chemical value. diagram confirms this opinion.

For Br=80, the atomic ratio is

$$r = \frac{188}{108} = 1.740\ 740$$

[TABLE 14.]

SYNTHESIS OF SILVER BROMIDE.

No.	Absolute Weights. Silver.	Bromide.	Analytical. Ratio.	Excess.
STAS.				
1	53.1958	92.6042	1.740 817	+77
2	51.3436	89.3780	782	42
3	55.0615	95.8505	790	50
4	55.8040	97.1450	825	85
5	48.3620	84.1904	838	98
Mean, 2-5	52.6		809	69
MARIGNAC.				
11	25.00	43.518	720	— 20
12	20.12	35.020	556	—184
13	15.00	26.110	666	— 74
Mean,	20		647	— 93

We really have only *one* point determined by Stas, wh 69 millionths above for 52 grammes of silver. Marignac, 1 average of 20 grammes of silver, found the point 93 mill below.

If we were to give equal weight to both analysts—which in this case would be unfair towards Stas, whose details we possess, while those of Marignac are not given in the works at hand—we would obtain, for about 36 grammes of silver, a point having the atomic excess—24, that is 24 millionths below the axis of abscissae.

Practically, the parabolic curve for Silver Bromide coincides with the axis of abscissae for the short distance for which we have any determinations.

But, for the reason stated, giving to Stas determinations in this case the greatest weight, we may conclude that the line representing the atomic excess of silver bromide is a parabolic curve above and very near the axis of abscissae.

D.—SYNTHESIS OF SILVER IODIDE.

For Io=127, the atomic ratio Iodide to Silver is

$$r = \frac{235}{108} = 2.175\ 926$$

The results obtained by Marignac (Clarke, p. 25) seem to be so discordant that we may omit them. The determinations of Stas corresponding to the sum taken in his "complete" syntheses are entered under B in the table, and are the upper points in the diagram. The curve shows a marked tendency towards the axis for moderate weights of silver; we might express this by saying that the *range* for Iodine is short.

If the atoms of sulphur, chlorine and iodine were used as projectiles, for the same amount of powder, the range of Io=127 would be expected to be much less than the range of a projectile weighing only about one fourth as much (S=32, Cl=35.5).

[TABLE 15.]

SYNTHESIS OF SILVER IODIDE. STAS.

No.	Absolute Weights. Silver.	Iodide.	Analytical Ratio.	Excess.	B.
1	97.5915	212.2905	2.175 297	—629	
2	43.5281	94.6894	362	562	
3	27.6092	60.086	271	655	553
4	39.8223	86.6653	306	620	534
5	24.4532	.....	.....	.....	560
6	38.0620	82.8375	383	543	493
7	136.2952	296.6240	385	541	497
8	82.3235	179.1590	294	632	639

SECTION III. THE DISSOCIATION OF THE CHLORATES.

Our old master Berzelius made use of the dissociation of potassium chlorate for the purpose of connecting the atomic weights of the chlorides with that of oxygen. His experimental determinations have, for a long time, been superseded by more recent ones; not because the results of Berzelius were less accurate than the modern ones, but simply because, in the absence of impartial criticism, fashion dominates in this branch of chemistry during the reign of the school of empirics. As a matter of fact, Berzelius found in 1826, that potassium chlorate left 60.851 per cent when heated till constant weight; forty years later, Stas found 60.843, or only 0.008 per cent less than Berzelius. In the main, Stas did not come nearer the truth than did Berzelius, as we shall see.

The theory upon which Berzelius introduced this process is simple enough, and the school of Stas has not corrected a single point thereof.

The formula of potassium chlorate is KaO_3Cl; when heated, it is said to lose all its oxygen, and to be reduced to potassium chloride, KaCl. Now, taking oxygen as the basis, say 16 exactly, chemists putting the analytical ratio

$$a = \frac{\text{Chloride}}{\text{Chlorate}} = \frac{\text{Residue}}{\text{Substance}}$$

assume the atomic weight of Chlorate=Chloride+48 and hence get the atomic weight

$$KaCl = 48 \frac{a}{1-a}$$

Having determined the analytical ratio of the dissociation, a very simple calculation would give the atomic weight of potassium chloride. Stas and his school have made this incidental process of Berzelius the basis of their entire system.

We may commend Berzelius for proposing and using this method, for he did pioneer work in this field of science, and never made this particular process a hobby; he remained steadfast in the practice of the simple processes, involving binaries mainly.

But by Stas and his school, this process has been made the corner stone of their entire system of atomic weights. The atomic weights in use to-day, all depend upon this reaction.

Now, at first sight, such a reaction is objectionable. It is too complex. We know, as a matter of fact, that potassium chlorate does not decompose in that manner exclusively. All know that perchlorate forms first; also that free chlorine escapes, and that some potassium oxide remains.* Besides, the reaction is almost explosive.

As to the calculation above indicated, it is therefore only an approximation. I have taken the trouble to indicate some of the most glaring errors in the calculation of the school of Stas†; but

*Van der Plaats, l. c., p. 509, states some of these facts; but that does not disturb him in his course.

†C. R., T. 117, p. 327; 1893

it is not worth while to enter upon details of that sort here. where it will be our business to examine *critically* experimental data only. If such examination shows that this process cannot give a value of precision for the atomic weight of potassium chloride, it is manifestly unprofitable to spend further time upon the method of calculation in common use.

We shall find by such examination, that this analytical ratio is *not* a constant, but varies very considerably with the amount of chlorate operated upon, and varies at a somewhat different rate according to the special conditions under which the dissociation takes place. But if the analytical ratio is a variable, the resulting atomic weight of potassium chloride will vary accordingly; that is, the atoms will weigh more or less according to the amount of matter taken!

While Stas made the dissociation of potassium chlorate the connecting link for all his atomic weights, he tried to make his method irresistible by combining this reaction with the corresponding dissociation of the bromate and iodate—especially those of silver. Thus, apparently different processes were used, to secure checks against constant errors. But the entire manner of procedure was irrational. The processes were, chemically, essentially identical, thus affording no check; they were altogether too complex to be suitable for fundamental determinations. The only positive result we are able to obtain from this mass of data, will be another demonstration of the general principle already sufficiently established, namely, that these analytical ratios are definite functions of the amount of matter operated upon.

We shall now, briefly consider, first the older and most common dissociation of potassium chlorate, and thereafter the dissociation of the corresponding silver salts.

A. THE DISSOCIATION OF POTASSIUM CHLORATE.

For the common atomic weights Ka=39 and Cl=35.5 we have, oxygen being taken as 16 exactly, the atomic weight of potassium chlorate 122.5 and potassium chloride 74.5; hence the atomic ratio for the dissociation is

$$r = \frac{74.5}{122.5} = 0.608\ 163$$

Subtracting this ratio from the analytical ratio, we obtain the analytical excess, as before.

We have, also in this case, carefully compared the authorities. Clarke gives again only ratios, no weighings. The results of Stas are taken from Aronstein, p. 249 and Van der Plaats p. 510. I have, of course, restored the original determination; what is called oxygen by these authorities, is simply the *loss* in weight of the chlorate. Hence the weight of chloride or residue is restored by subtracting this "loss" from the weight of chlorate taken.

The data of the experiments of Berzelius and Marignac we take from Sebelien (p. 71 and 77). For Nos. 7 and 9 the weighings give a different ratio from the one stated by Sebelien. Now, since the ratios given by Sebelien agree with those given by Clarke (p. 11), who claims to have revised all, it is proper to accept the ratio as correct.

In Stas results, Aronstein p. 249, the weight of the oxygen in No. 13 by a misleading misprint is one entire gramme in error.

The data obtained by Berzelius in 1826, by Marignac in 1842 and by Stas in 1860 are given in the following table:

[TABLE 16.]

DISSOCIATION OF POTASSIUM CHLORATE.

No.	Absolute Weights. Chlorate.	Chloride.	Analytical Ratio.		Exc
BERZELIUS, 1826. Dry Way.					
1	10 to	.....	0.608	54	
2	15	.....		50	
3	grammes	.....		50	
4	.....	.....		51	
MARIGNAC, 1842. Dry Way.					
5	46.850	28.506	0.608	451	
6	32.590	19.826		350	
7	37.554	22.839(?)		330	
8	73.733	44.862		439	
9	68.640	38.718(?)		390	
10	64.690	39.357		394	
STAS, 1860. Dry Way.					
11	69.873	42.5094	0.608	381	
12	82.126	49.9648		406	
13	86.501	52.6305		437	
14	132.923	80.880		472	
15	127.2125	77.4023		449	
STAS, 1860. Wet Way.					
16	59.727	36.344	0.608	502	
17	95.7975	58.2955		529	
18	147.318	89.634		439	

The simple consideration of the numerical data of Table show that none of these analytical ratios are independent of amount of chlorate used. By combining the experiments which nearly the same weight of chlorate was employed, obtain the following results.

MARIGNAC, No.	6, 7	5	8, 9, 10
Weight used,	35	47	69
Analyt. excess,	177	288	245
STAS, dry—No.	11	12, 13	14, 15
Weight,	70	84	130
Excess,	218	260	297
STAS, wet—No.	16	17	18
Weight,	60	96	148
Excess,	339	366	276

More strikingly this is shown by Figure 4, the lower diagram of Plate II, which will be readily understood. In this, the experiments of Marignac and Stas in the dry way might have been represented by one single curve; but since the conditions were somewhat different, we have represented each set by its own curve. The mean of each series has also, been represented by a double mark.

The wet way process is represented by a curve quite distinct from that representing the dry way determination of Stas. For the latter, the maximum occurs at about 150 grammes, while the wet way process gives its greatest excess for 100 grammes already. In other words, the range of the parabolic curve for the dry way is greater than for the wet way, though the latter shows a greater angle of elevation.

The determination of Penny (1839) made in the wet way, fall exactly into line with those made by Stas twenty years later.

The records furnish the following additional determinations made by other chemists.

[TABLE 17.]

DISSOCIATION OF POTASSIUM CHLORATE.

Ratio.	Analytical	Excess.
PENNY, 1839, Wet Way.		
0.608	25	9
	22	6
	15	−1
	20	4
	23	7
	30	14
PELOUZE, 1842. Dry Way.		
0.608	43	27
	57	41
	30	14

Ratio.	Analytical	Excess.
GERHARDT, 1845. Dry Way.		
I. Series, 0.608	71	55
	81	65
	75	59
II. Series, 0.609	47	131
	47	131
	52	136
MAUMENÉ, 1846. Dry Way.		
6.607	88	−28
	90	−26
	93	−23
	91	−25
	85	−31
	95	−21
	95	−21

It is very instructive to notice that while Gerhardt's first series showed an excess about double that of the best determinations, it jumped to five times that value when he increased the complexity of his apparatus with a view to obtaining more accurate values. The same thing happened to Ditmar when trying to diminish reputed errors of Dumas in that way.

Maumené made special efforts to avoid getting values that were too high—and succeeded admirably, by dropping out in the opposite direction. Thus we have, in units of fifth place,

Marignac, mean	23
Maumené, mean	−25
Mean of both	− 1

This would practically bring us the atomic ratio exactly.

But we no not like this popular method of determining fundamental data by discordant means of concordant determinations.

It is quite apparent, that the dissociation of potassium chlorate, for the purpose of the determination of atomic weights, has an extended history.

The following table presents this remarkable history in the simplest possible manner, by giving the leading data in chronological order.

Chemist.	Year.	No.	Mean Values. Weight.	Excess.	Probable Error.	Way.
Berzelius,	1826	4	12.5	35	0.6	Dry.
Penny,	1839	6	5	6	1.4	Wet.
Marignac,	1842	6	54	23	1.3	Dry.
Pelouze,	1843	3	.....	27	5.3	Dry.
Gerhardt.	1845	3	.....	60	2.0	Dry.
Gerhardt,	1845	3	.....	133	1.1	Dry.
Maumené,	1846	7	27	−25	0.9	Dry.
Stas,	1860	5	100	26.5	1.2	Dry.
Stas,	1860	3	100	33	1.7	Wet.

The least average weight of chlorate used in one determination was 5 grammes, by Penny; Stas with 100 grammes, averaged the highest — in weight used.

As to analytical excess found, Maumené averaged as high negative as Stas, Marignac and Pelouze on the other side — all in the dry way.

Stas, in the wet way, found almost as high an excess as Berzelius in the dry way — in the first determinations ever made.

The column of "probable error" is particularly instructive, especially for those who may yet have an idea that possibly this quantity is of some slight value to judge the chemical importance of the mean found. In order that we may not be blamed for having selected or in some way produced the *probable* errors

here stated to illustrate the absurdity thereof, we will add that the numbers are simply copied from Clarke (l. c., p. 13).

The only values exceeding 2 are those of Pelouze and Gerhardt, I. Series. We will admit that a simple inspection of the individual numbers of Table 17 would also tell us that much.

Next, the smallest probable errors belong to the determinations of Berzelius and of Maumené. The former, being the first attempt made, are admittedly too high; the latter is the only series giving negative values of the excess — and all chemists have unisono condemned this work of Maumené.

All the other "probable errors" range from 1.1 to 1.7 units in the fifth place. The smallest, 1.1, marks that most outrageous 2nd series of Gerhardt, the most absurdly out of the way of all attempts made. The probable error of Stas in the dry way (1.2) comes next to this work of Gerhardt, and is succeeded by that of Marignac (1.3).

In the wet way the work of Penny shows a smaller probable error (1.4) than that of Stas (1.7).

It would indeed seem that this series of probable errors had been especially manufactured to show the utter chemical absurdity of the whole method of the least squares, as applied by Clarke, Ostwald, and Van der Plaats, and that a little less show of mathematical learning, would have been particularly desirable in the treatment of this question of Chemistry.

The large number of determinations made by several chemists gives us a chance to examine the general influence of quantity on accuracy in this kind of work. We have referred to the examination of Ostwald (see p. 30), who from Stas' determinations, tested by the methods of the least squares, arrives at the conclusion, that the precision of the results increases with the amount operated upon. Since, however, the least squares have been shown to be not legitimately at home in Chemistry, the resulting probable errors being not only useless but absurdly

misleading, the conclusion of Ostwald has nothing to rest upon, and we may consider the question entirely open.

As to material. we have four series of precision, namely the two of Stas, and the one each of Penny and Marignac. These four series divide themselves into two equal groups according to the method used, namely two series of wet way determinations (Penny and Stas) and as many series of dry way determinations (Marignac and Stas).

The data given, in Tables 16 and 17, have been represented in Figure 5 as function of the mean weight of the material used;

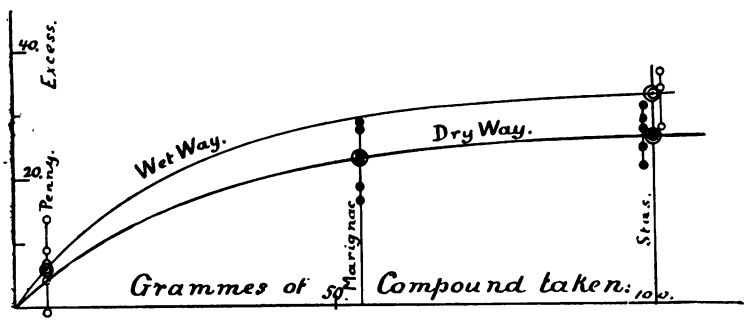


Fig. 5.

that is, the abscissa represents the mean weight used, namely 5 grammes in the determinations of Penny, 54 grammes in those of Marignac, and 100 grammes as the mean weight of potassium chlorate employed by Stas in each one of his determinations. In the diagram, each individual result obtained is represented by a circle (wet way) or an equally large black dot (dry way); also the means have been marked by an extra outer circle. The ordinate is the analytical excess found in each determination, represented by units in the fifth place, as usual.

It is evident, that the dry way determinations mark a parabolic curve, and that the wet way determinations fall on a like curve with a somewhat greater elevation at the origin.

This diagram shows plainly, that the use of greater quantities

is a positive disadvantage, for the analytical excess increases with the amount used. We have continually met with this fact, but here have an opportunity of presenting it without disturbing details.

We also notice that the range of the individual determinations in the case of Stas is but a trifle less than in that of his predecessors. Though the absolute range for the early determinations of Penny is rather larger than that of the pretentious work of Stas, it is marked by only one case at each extremity, while the bulk of the determinations of Penny fall close to the mean.

Surely, the use of large quantities carries us necessarily away from the truth we are seeking to find. The entire plan of research, mapped out by Stas, was a stupendous blunder. Stas has led chemists into a desert and kept them aimlessly wandering about therein for nearly forty years.

The first determinations, those of Berzelius, cannot be compared in this connection; they may be utilized, however, in a final historic retrospect. The analytical excess in the dry way is, according to the determinations of Berzelius of 1826, equal to 35; it reached its lowest point in 1842 when Marignac's researches brought it down to 23; the work of Stas ran it up to 26.5 again. In the wet way, Penny came nearest to the atomic ratio, his mean exceeding it by six hundred thousandths only. Stas, on account of the large masses operated upon, gave the highest value, 33, five times the departure of Penny's determinations.

B. DISSOCIATION OF SILVER SALTS.

Stas prepared the chlorate, bromate and iodate of silver, and subjected them to the Berzelian operation for the purpose of checking the work on potassium chlorate for chlorine, and to

furnish corresponding equations for the determination of the atomic weight of bromine and iodine. The dissociation would give the atomic weight of the binary compound left, and a determination in the wet way gave its relation to silver; from these two, a simple *algebraic elimination* gave each atomic weight separately. As we have been compelled to give a good deal of critical detail on the important syntheses of Stas, we may be excused to omit a detailed consideration of the many hypotheses involved in the use of this apparently simple mathematical determination of atomic weights. Even those chemists who may think that the numerous flaws of this universally admired process of Stas ought to be shown up in detail—if they really exist—must be satisfied by a reference to the next section, wherein they will see that even if there were no magnificent flaws in this process of elimination, the wet way determinations used are absolutely without chemical value. It cannot be expected that I should show up in full detail ALL the curious errors in fact, in chemical processes and in conclusion, that combined have brought error and confusion into the highest branch of chemical science; I have limited this exposition of my critical examination to the most essential points, which necessarily decide the entire question at issue.

For the determination of the analytical excess, we need the atomic ratio. The common atomic weights being Br 80, Io 127, the atomic ratios for these *silver* salts are

$$\frac{\text{Chloride}}{\text{Chlorate}} = \frac{143.5}{191.5} = 0.749\ 347$$

$$\frac{\text{Bromide}}{\text{Bromate}} = \frac{188}{236} = 0.796\ 610$$

$$\frac{\text{Iodide}}{\text{Iodate}} = \frac{235}{283} = 0.830\ 389$$

The numerical data of the determinations are given in Table 18, in the usual order.

[TABLE 18.]

SILVER CHLORATE.

No.	Absolute Weights. Chlorate.	Chloride.	Analytical Ratio.		Excess.
19	138.7890	103.9795	0.749	191	—156
20	259.5287	194.4435		218	—129

SILVER BROMATE.

	Bromate.	Bromide.			
21	86.5457	68.9310	0.796	469	—141
22	101.9875	81.2361		530	— 80

SILVER IODATE.

	Iodate.	Iodide.			
23	98.2681	81.5880	0.830	259	—130
24	156.7859	130.1755		276	—113
25	76.5561	63.5600		241	—148

The graphical representation is given in Figure 4 of Plate II. For the silver chlorate we have only two points, indicating the descending branch of the usual parabolic curve. The only two points on the bromate curve seem to mark the highest point in the same. For the iodate, we have three points, determining the parabolic curve very well.

Though but few points in these trajectories are determined, it is quite apparent, that the elevation of all is much less than that for the corresponding curves for potassium chlorate, while the range—in the sense of the flight of a projectile—is greater. This is directly connected with the greater fixety of silver (108) than potassium (39). For the same metal, the iodate shows shorter range than the chlorate, as in the corresponding synthesis of the binaries.

SECTION IV. VOLUMETRIC ATOMIC WEIGHTS.

This title is an intentional absurdity. It fitly designates the method, introduced by Pelouze, used by Dumas, made prominent by Stas, and developed by a young american chemist so admirably that he happily can declare it "hopelessly troublesome." The method is condemned by the famous rule of Berzelius, (p. 16, supra); for in this process, the skill of the chemist is everything, the scientific principle nothing, exactly as in the feat of the rope dancer: the skill of the artist is everything, scientific mechanics nothing. This method also conflicts with my own first rule, (pp. 71—72), that we must possess the exact weight of the body in question; for in this process we know not even what body really is present, what it is that has been weighed—not in simple, tangible form, but as it were, by implication.

We may admire the skillful cook who prepares the excellent soup—but the chemical laws involved in his art are too deep for science. So it is with the *Consommé Pelouze*, improved by Stas and brought to the highest possible perfection by Richards.

Having neither time, nor space, to waste on such a thing, let us simply look at it historically.

Stas published twenty-one determinations of this kind in 1860; wonderfully concordant results were obtained for the ratio between silver and potassium chloride (Aronstein pp. 256-257). These identical determinations form the second link in the chain of Ostwald's calculations (l. c., p. 32), the first being the dissociation of potassium chlorate (see p. 43, supra). He gets a "probable error" of only 0.0003, that is three ten thousandths on the atomic weight of silver, or less *than 3 millionths per unit!* Wonderful, admirable is the accuracy of the work of Stas and great is the chemico-mathematical skill at the University of Leipzig! It is really cruel to disturb these dreams of the cory-

phees of chemistry of the school of Stas—by calling them back from their flights of fancy to the laws and facts of "experiment,

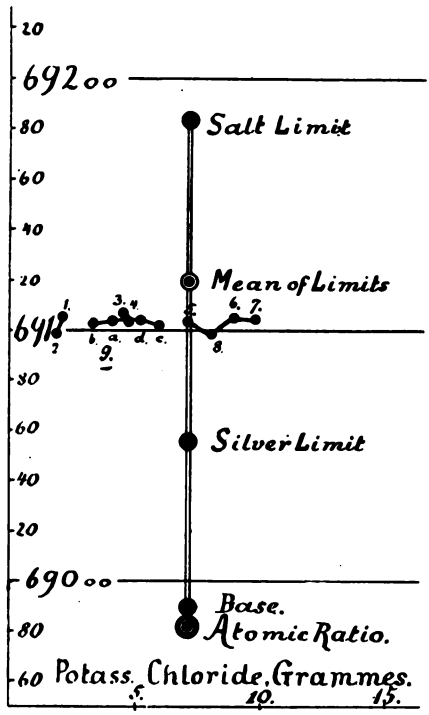


Fig. 6.

measure and calculation."—*In Figure 6*, the results of the first 9 determinations in question are represented; for 9, four cases, a, b, c, d, are given. The vertical scale of the diagram is large, the oscillation of the dots small—thus beautifully representing the *wondrous concordance of the determination of Stas, that has hypnotized modern chemists for over thirty years.*

While the chemical world was wrapt in admiration of these results, the annals of chemistry contained already an antidote in the researches of *G. J. Mulder* on the assay of silver, published

at Rottersdam in 1857. Now Stas was chemist of the mint at Brussels, and ought to have been well posted on this important work in his special line, issued in his immediate neighborhood. However, it was not till 1872 and 1874 that Stas studied this subject carefully. In his first paper of 1860 he had only in a general way referred to this matter at the close (Aronstein p. 59) as a constant error of small moment. Now, in 1872, he recognizes the fact that silver chloride, whether in pulverulent or curdy state, is markedly soluble in water, up to 13 milligrammes per liter; but that *it is completely precipitated by an amount of a soluble chloride three times that which is dissolved.* See Van der Plaats, (l. c., p. 511). Also, Richards, Zeitschrift anorg. Chem., VI., p. 105; 1894.

Accordingly, Van der Plaats* has, in 1886, completely disregarded the entire series of 21 determinations which, however, continue to form the basis of the atomic weights of Oswald in 1891. Stas himself, in 1882, has given to the world a few new determinations, which are taken by Van der Plaats (l. c., p. 513) instead of the discarded determinations of 1860 which still hold Ostwald spellbound.

The total number of these few determinations — Stas 1882 against Stas 1860 — is four, in two pairs, made according to *two* different *methods.*

The two determinations according to the first method were made with almost identical amounts of matter, and hence gave

* It is funny to notice some of his involuntary expressions of perplexity, (l. c., p. 512):

"I cannot conceive why the ratio found in 1860 or 1865 has always been *below* that of 1882, nor why the difference reaches 3 ten-thousandths for potassium chloride and is almost zero for the chlorides of sodium and ammonium. However that be, the determinations of 1882 are the most exact and the only ones I have admitted in my calculations."

Now this inconceivable discrepancy is one-third of a thousand — not a small matter. So he throws the "admirable work" of 1860 and 1865 overboard, and relies on the couple of much "more admirable" determinations of 1882.

almost identical results; we will give the means only (Van der Plaats, l. c., p. 513).

The amount or potassium chloride used is 7.07778 to the hundredth of a milligram — very fine, indeed. The amount of silver equivalent hereto was found by the process:

At the salt limit,	10.23040 grammes.
At the silver limit,	10.24940 grammes.
Showing a difference of	0.01900 grammes.

which amounts to almost exactly two milligrammes per gramme of silver; *that is, an error of one in a thousand.* A very different rate from 3 in a million above stated by Ostwald.

The analytical ratio, that is the amount of chloride per unit of silver, is therefore:

At the salt limit*,	0.691 838 5
At the silver limit,	0.690 556 0
Difference,	0.001 282 5

These two limits are entered on Figure 6. The "salt limit" is the point at which the silver precipitation is apparently completed. But if now the amount of chloride used (0.692 nearly per unit of silver) were actually combined with the silver originally in solution, then the addition of a few drops of silver solution could not produce a precipitate; but in fact, precipitation *is* produced, and silver solution may be added till the "silver limit" is reached — so that about 0.691 of chloride would be equivalent to a unit of silver. But this is false also for upon adding chloride, a precipitation again occurs till the salt limit is reached. This see-saw can be repeated indefinitely.†

As a plain matter of fact, this reaction in the wet way involves an *uncertainty* of fully one-tenth of one per cent; and at no time

* Van der Plaats gives *these seven* digits! He is very exact — in form.

† But in varying absolute amounts, see Richards, Zeitschr. anorg. Chemie VI, p. 118; 1894.

in that big *belt of uncertainty* between the silver and salt limit, have we any *positive knowledge* of what chemicals we really do have in that pot of soup. In fact, our advanced modern chemical theorists, amongst whom Ostwald is recognized as a bold and brilliant leader, hold that, in the presence of water, all compounds are partially decomposed into their constituents, which they call the ions. Accordingly this *Consommé-Pelouze* contains ions of silver, ions of chlorine, ions of potassium, also potassium chloride and some silver chloride in solution, as well as a large amount of silver chloride in solid form. Now, who can tell *exactly* what this is?

Stas and his followers *declare* that the *mean* between these limits is, *of course*, the exact point. See the figure. They then calculate that mean, with their customary precision — Van der Plaats obtains as "terme moyen" or

Mean..... 0.691 197 2

This calculation is correct, to the seventh place, or the ten-millionth part; this figuring is perfectly exact, as anyone can readily ascertain by figuring it over. The figures do not lie — they cannot do that.

But when Van der Plaats, or Stas, or any other chemist, asserts that these figures represent the analytical ratio between silver and potassium chloride in a chemical sense or that *one gramme of silver requires the chlorine of 691.1972 milligrammes of potassium chloride to become completely converted into silver chloride* — then they simply make an assertion about the truth or falsity of which they give no experimental scientific demonstration whatsoever. A careful chemical examination shows that their statement is entirely false in every particular, and that it is so according to their own experimental data.

For the determination of the solubility of silver chloride by Stas would seem to prove, that the "salt limit" contains an *ex-*

cess of potassium chloride exactly *three* times the equivalent amount of the silver chloride soluble in the bulk of water used; hence that we should take the point marked "base" on the diagram, to represent the condition of this liquid or "chloride-ion" soup in which the entire amount of silver present is actually in the solid form as silver chloride. In other words, that this excess, from the base to the salt limit, represents the army of potassium chloride atoms and ions necessary to keep the silver chloride entirely out of the soup — and in the solid form only.

Now this base point is almost identical with the point marking the atomic ratio; for Ka=39 gives the ratio

$$\frac{\text{Potass. Chloride}}{\text{Silver}} = \frac{74.5}{108} = 0.689\ 815$$

while the determinations of the two chemical PHASES or points by Stas gives — for six decimals *only* —

Salt limit	0.691 839
Silver limit	0.690 556
Difference	0.001 283
Half difference	0.000 641 5
3 times half difference, or excess	0.001 925

Hence,

Salt limit	0.691 839
Excess required	0.001 925
True Base	0.689 914

Now, this agreement of the base with our atomic ratio is surely close enough. But since Van der Plaats (l. c., p. 513) shows that the value of Stas is a trifle too high, on account of the potassium chloride containing between 2 and 2½ parts of silica per hundred thousand, we may apply the correction calculated by him, namely 0.000 0157 which we may be permitted to round off to six decimals, which gives

Base calculated	0.689 914
Too high, impurity	0.000 016
True base, pure salt	0.689 898
Atomic ratio	0.689 815

This agreement is perfectly satisfactory to us. With this, all the fine conclusions of Stas are overthrown, (Aronstein, p. 59). He has not established a single fact in conflict with the unity of matter.

It is not worth while to study the second method — of equal cloudiness about the Mean of Limits. We have studied the cloudiness of the Stasian Chemists more than we desire to — and, we trust, sufficient to understand the cause of this cloudiness.

The silver and chloride reaction in the wet way shows well marked phases. These phases have been carefully determined since Stas' first and second publications, which have been superseded — except in Leipzig — by those of 1882. These last determinations exactly conform to the atomic ratio calculated by us from the common atomic weights, i. e., the Proutian numbers, if we may say so.

But it is useless to waste further time on this topic. It has been and must be misleading to use such reactions as these in the wet way, for the determination of atomic weights chemically. We do not know exactly what is going on in such a soup, nor what we really have present therein. For the purpose of determining the atomic weights of the elements, we must have definite compounds, in weighable form.

The school of Stas seems to have, in its practice, considered the determination of the atomic weights mainly an exercise in mental gymnastics, combined with chemical gymnastics, akin to what rope dancing* would be in a laboratory of physics. We

* In 1891-2 the Board of Harvard University arranged their Chemical Laboratory admirably for this work. — Richards, Zeitschr. anorg. Chemie, III, p. 469: 1893.

should in the future, confine ourselves to "experiment, measure and calculation," and thus avoid to bring the highest branch of our noble science again into disrepute and confusion.

Our critical examination having removed the determinations of potassium, sodium and lithium from consideration, it is not worth while to examine the mixed reactions between chlorides and nitrates of which Stas has made so much. We are heartily tired of this partly negative work. But it had to be done. Not only had the obstructions to be removed, before a new building could be erected, but we had to examine the material carefully in order to preserve such parts as can be put to use n the new structure.

Before we begin this work of construction, we must examine some of the recent work done in the school of Stas. We select one of the most noted contributions from that school, namely the determination of the atomic weight of copper, by Prof. Richards of Harvard University near Boston. We copy an article which we sent to the editor of the *Chemical News*, London, and which appeared October 6, 1893, in that Journal. Essentially the same article was also published in Zeitschr. anorg. Chemie, Bd. V. p. 293—298; 1893.

SECTION V.—DETERMINATION OF THE TRUE ATOMIC WEIGHT OF COPPER.

"Chemistry of precision is at present in a very peculiar condition, especially that branch thereof which has for its object the determination of the atomic weights of the chemical elements. On the surface it seems that this department is in a most flourishing condition; the number of determinations never was greater than at present, the space devoted to this topic in the chemical periodicals never was more extended, and the accuracy of the

"results is stated with an astonishing degree of precision, quite often expressed by means of refined methods of calculation, such as we formerly used to meet in astronomy only.

Under such conditions it is exceedingly unpleasant to be in duty bound to present an abundance of facts which demonstrate that all this glory is but a hollow mockery and a sham, and it even becomes difficult to obtain a hearing for the purpose of submitting these facts for examination. Since the very renown of Stas depends upon the failure of chemists to practice mathematical and chemical criticism, it can scarcely be expected that these faculties will now respond promptly to our call after having been dormant for a quarter of a century. Our modern chemist seems to be as unwilling to find errors in the work of Stas as philosophers were to look through the first telescope for spots on the sun.

Nevertheless the recorded facts show that the eminent analyst of Brussels has entangled the entire subject of the atomic weights in a web of systematic errors both chemical and mathematical, and has besides committed some of the most astonishing errors in the detail of his work.

However unwilling chemists may be to look doubtingly at the work of their recognized master, it seems worth trying to make them join us in the critical examination of the work of a disciple of the school of Stas. To bring it more nearly home to the chemical public of this day and of this country, let us select for such examination the work of recognized merit recently completed by an American chemist according to the general methods of Stas, with the single exception of the use of enormous quantities, which much-extolled peculiarity of Stas was one of the worst features of his system.

In looking over the entire field, I can find no example more fair for this critical examination than the work of Professor Theodore W. Richards on the atomic weight of copper. This

"work has been republished in full in Germany, in the new *Zeitschrift für Anorganische Chemie*, Bd. I., 1892. The results thereof have been accepted as practically final by Ostwald (*Zeitschrift*, ix., p. 383, 1892), who is generally recognized as an authority on the subject of atomic weights. I will further add that I have the highest regard for the analytical skill of Prof. Richards, who has spent on this work four years of his time in the best appointed laboratory of research in America.

If therefore I am constrained to declare that the final results of Prof. Richards are without permanent value to chemistry, being nearly one-fifth of one per cent. in error; that, moreover, this entire research was superfluous, because a more accurate determination was known before this work was published; and that finally the only two reliable results which he obtained in his laborious research were not recognized by him as such, but were with great labor and much chemical acuteness blotted out from his work by himself; if I shall be compelled to declare all of this, I shall equally insist that the fault thereof is not in the excellent chemist personally, but is due to the school, the system of Stas which he represents.

To keep this paper within reasonable bounds, it will be necessary to proceed directly to the determination of the atomic weight of copper; thereafter the critical part can be very briefly given.

The electrolytic ratio 2Ag: Cu is 3.402, if we adopt temporarily 63.5 as the atomic weight of copper, and take Ag at 108 as standard. For 63 and 64 the ratio would be 3.375 and 3.438.

Now the determinations of Shaw (1886) gave 3.400; Lord Rayleigh found 3.404 to 3.408, and Gray 3.401. These values are almost identical with the one corresponding to 63.5 as the atomic weight of copper. This therefore *is* approximately the value sought. It only remains to find the minute deviation of this number from the true atomic weight, or to establish that this deviation is zero.

"The mean value given by Richards himself is Cu 63.61, resulting from the means of all his eleven series, oxygen being taken as 16.000. Of course this mean involves the use of several of the erroneous values of Stas; but as in the different series the elements employed are different, it is impossible to make allowance for these errors in the general mean. Part of the variation of the individual means is due to this fact; they run from 63.593 to 63.641. The actual range of these means is 0.048, or say 0.05.

Professor Richards next throws out six of his eleven series, and thereby reduces the range to 0.008, or say 0.01 in the means of the series retained, and gets 63.604 as a sort of selected final mean. This is a tacit admission that more than half of his series were made according to methods not fit to yield results of precision. This final selection of the best agreeing results is quite generally practiced in the school of Stas to-day. Thus Van der Plaats freely omits entire series of Stas, according to his own sweet will and pleasure (*Annales de Chemie*, vii., p. 512; 1886). The most glaring example of the kind—a genuine parody on sound science—may be found in Van Laar's "Thermodynamics" just published (p. 8). Having tabulated the results obtained by the different chemists—and he seems to consider the determinations of Leduc and Lord Rayleigh as legitimate determinations of atomic weights—he says drily, and with absolute unconcern, "If we except the value under *a* as being certainly too low, and those under *d* and *e*, which are certainly too high, we get, as mean of the values under *b* and *c*, 15.881—exactly the value of Morley. For O=16, then follows H=1.0075." This work is highly commended in a Preface by van't Hoff, and has been equally highly recommended by Ostwald. The selection made by Richards, therefore, is in keeping with the practice of the school, for which it would be unjust to blame the individual.

Next the question arises, is the value 63.61, or say 63.60, of Richards, the true atomic weight of copper? In that case the

"deviation of 63.5 would be 0.10. But the determinations of Richards showed a range of 0.05, which is exactly half of the quantity in question. No scientist will pretend that a quantity is established with precision when it is affected with an uncertainty of half its own value. In other words, the work of Richards has *not* established the atomic weight of copper at 63.6.

A careful examination of the methods used by Richards in his eleven series compels the condemnation of ten thereof as unfit for the purposes of precision. Only the use of *blue vitriol* as material, and the electrolysis and dissociation thereof, remain as legitimate processes for the determination of atomic weights. Of such determinations Richards has made three excellent series. The results obtained, expressed in parts by weight in hundred thousand, are as follows, the reference page being to the German edition:—

Series	I.	II.	III.
Page	162	168	171
Copper	25455	25450	25448
Water	35958	36067	36067
At degrees C	250	360	370

Professor Richards also determines the amount of sulphuric acid left after electrolysis; it is the ghost of Stas demanding the famous *complete analyses* at the expense of precision. Richards uses a *volumetric* process for this purpose, involving two indicators, also pure sodium carbonate, hence demanding the exact value of the atomic weights of sodium and of carbon. Such complex processes will give concordant results in so skilful hands as those of Richards; but the unknown residual errors make the final result useless in chemistry of precision.

Now right here Prof. Richards loses himself in the labyrinth of Stas. Summing up the three ingredients determined, Richards finds a deficiency of *five* in *ten thousand* outstanding. In other

"words, 1 mgrm. of blue vitriol in every 2 grms. has been lost—a quantity entirely too large to be overlooked in chemistry of precision.

Not knowing that volumetric processes can claim no place in the determination of the precise value of atomic weights, Prof. Richards thinks his sulphuric acid determination right; he is properly certain of his copper determination; hence he concludes that the error can only have occured in his determination of the water of crystallisation. He now pushes the heating of the blue vitriol to the dissociation of the sulphate. He reaches a dark red heat. He thus has secured that elasticity which Stas utilized in the precipitation of the silver chloride, and which Richards alone has properly condemned in his work on the atomic weight of barium.

However, Professor Richards is too good a chemist to hide for himself the very unsatisfactory outcome of this search for the missing substance. He admits the absence of the necessary *evidence*, but says: "There is no doubt of its great probability." This is one of the classical phrases of the school of Stas. It has absolutely no place in the chemistry of precision.

Professor Richards adds:—"Upon such a matter it is difficult to see how more definite results could have been obtained." He does not know that he had the most definite and admirably exact results when he started out on this chase after the lost water, not dreaming that it was the acid that had been lost by him. He thus throws away the only valuable determinations of his four years of work. But, also, this stupendous error is due to the school he follows.

To show this in the shortest manner possible, let us adopt the atomic weights of H=1 and S=32, established by my limit method, and also put Cu=63.5; the analysis thereafter will show how much the "deviation" of this atomic weight amounts to. Thus the formula—

$$CuO_4S+5H_2O$$

"for the atomic weights specified requires per hundred thousand parts of blue vitriol—

Copper	25451
Water	36072

It is plain that these calculated values are practically identical with those found by Professor Richards given in the preceding pages. The correction to be applied to the observed values to obtain the calculated values are—per hundred thousand parts of blue vitriol—as follows:—

Series	I.	II.	III.
Copper	—4	+1	+3
Water at 360°		+5	+5

The agreement is remarkable; the error of the determinations is only *one milligrm. in twenty-five grms.* if we take 4 as the mean of the above numbers. Thereby these determinations of Richards stand in the front rank of atomic weight determinations. That he failed to see this and started upon the long chase for more water is exclusively due to the dense fog that for a quarter of a century has been darkening this entire field of chemistry, so that at present, not only the old, but also the young chemists seem to have lost the faculty of sight in the broad light of day, and refuse to look at truth.

Thus it is established by these two determinations of Richards—the only two accurate ones in his entire research, but which he himself, as faithful Stasian chemist, had corrected away from truth—enable us to assert that the deviation of the true and exact atomic weight of copper from 63.5 is certainly not over 0.002.

A series of determinations carried on in accordance with the conditions of my limit method will no doubt show that *the atomic weight of copper is exactly* 63.5 in the mathematical sense.

In conclusion, I beg leave to express the hope that the young chemists—at any rate, those in this country—will no longer take

"part in the blind worship of an authority that has covered the immortal work of Dumas and Berzelius with the rubbish of a spurious accuracy and an imaginary analysis, and hereafter rather assist in the determination of the true and exact value of the atomic weights of the chemical elements."

WHERE THAT SULPHURIC ACID DID GO TO.

To complete the critical examination of the work of Professor Richards, on blue vitriol, I had written quite an elegant article, in which I showed where that sulphuric acid did go to; but I have withdrawn it, because his work has already received more attention from me than it deserves. When I published my critical examination of the determination of the copper in the article reprinted above, I rather expected that Professor Richards might profit thereby, and from a mere performing chemist gradually develop into a real chemist, who can think chemically as well as do some nice manual work in the laboratory and watch the oscillations of the pointer on a costly balance. It does not seem that his general preliminary scientific education has been sufficiently broad to enable him to comprehend my kind criticism; hence I shall no longer thrust my benevolent attentions upon the young professor. He appears to depend on the honor and renown of the grand old institution that has favored him with the best laboratory facilities in America, rather than to bear in mind, that the renown and standing of even the best institutions are but a reflex from the sum of the labors of distinction that its professors have accomplished. — Zeitschr. anorg. Chemie, VI, 102; 1892.

I will here only say that Professor Richards ought to have paid some attention to the Science of the Laboratory bearing on the production of persulphate by the electrolysis of sulphates. The first discovery, by Berthelot, dates back nearly twenty years; his more detailed publications were made in 1891, in refutation to the German chemical radical "SULFURYLHOLOXYD" of Traube.

Now every one atom of persulphate formed represents the saturating power of two atoms of sulphuric acid. To determine the amount of sulphuric acid in the solution of blue vitriol by volumetrically measuring the saturating capacity after the electrolysis has, by changing $2f$ atoms of sulphate to f atoms of persulphate, reduced that capacity f atoms, represents a string of chemical hypotheses and unwarranted conclusions rivalling those of Stas operating the Consommé Pelouze. In Exp. 4, p. 165, Richards has lost 51 atoms of every 100,000 of the acid, or one milligramme in every two grammes. That is, certainly, an amount far above the pretended precision of the performing chemist of Harvard. — See p. 133, line 1.

Thus Professor Richards tries to determine the water that was not there, because it happened to be sulphuric acid. He failed to find the sulphuric acid that was there, because before determining it, he ignorantly changed a variable fraction thereof into persulphuric acid of half the original saturating capacity, and then tried to determine the total amount volumetrically as sulphuric acid by its saturating capacity only. By these astonishing blunders, the earmarks of a most appalling empiricism, he had so distorted the percentages that even his true determination of the copper present, was falsified in his calculation.

This sort of work is being applauded as chemistry of precision, and in such manner the followers of Stas determine atomic weights!

In conclusion I wish to assure my readers that it is only upon compulsion, and solely to establish the truth and expose sham science, that I enter upon these critical examinations. I entertain no personal enmity towards any of these men and freely adopt the words of the great Reformator:

Niemand wolle sich zu mir Hass oder Ungunst versehen, denn mein Muth ist zu fröhlich und zu gross dazu, dass ich jemandem herzlich möchte Feind sein: ICH HABE AUCH NICHTS FÜR AUGEN, ALS DIE SACHE DER WAHRHEIT AN IHR SELBST, DER ICH AUS HERZEN HOLD BIN.

PART SECOND.

DETERMINATION OF THE

TRUE ATOMIC WEIGHTS

OF THE

CHEMICAL ELEMENTS.

CHAPTER I.

GENERAL PRINCIPLES.

The chemical atom is the smallest amount of matter that enters into chemical combination with any other particle. *It is, therefore, impossible to determine the atomic weight except by a chemical process.*

Certain physical laws may furnish the chemist with most important indications as to the particular *multiple* of the combining proportion determined by analysis, to be accepted as the atomic one; but the real determination of the *exact weight* of this quantity can be furnished by a chemical process only. It is the chemical union that decides what is the chemical atom.

It is true that even Berzelius has made use of purely physical processess for such a purpose; but the atomic weights thus obtained cannot be recognized as the weight of chemical atoms.

The same remark applies to recent endeavors of this kind. Thus, the so-called System of Atomic Weights of Le Duc (Comptes Rendus, T. 116, p. 383; 1893.) can receive no recognition in chemistry. The weights he tries to determine are not selected by the fundamental property of chemical combination.*

* Prof. G. Krüss of the University of Munich does not understand this fundamental point—or he would not have associated my atomic weights with those of Le Duc. Jahrbuch der Chemie, 1893, p. 49.

Whether the results of such physical determinations agree or not with chemical research is of no particular importance in chemistry.

The only legitimate method of determining the atomic weight of any chemical element or radical F is by forming or decomposing its combination with the chemical element or radical the atomic weight D of which is known.

If the compound D + F is formed, the process of determination is a *synthesis;* if it is decomposed, the process is an *analysis.* Special chemical and physical conditions will determine which one of these processes is to be preferred in any given case.

In the famous combustion of the diamond by Dumas (p. 21) the carbon was weighed as diamond, and the product of combustion was also weighed.

Hence the F of our general formula represents the diamond burnt, and D the two atoms of oxygen combining therewith; but this latter could only be determined by difference, by weighing the product of combustion.

ONLY SUCH PROCESSES OF DIRECT SYNTHESIS OR ANALYSIS OF SIMPLE COMPOUNDS CAN LEAD TO EXACT RESULTS. A brief consideration of the theoretical and experimental details of such a process will demonstrate that all other more complex and even indirect reactions which have been freely used in the past, must be entirely discarded in the future.

The weight q of the substance, the atomic weight of which is known or assumed as standard, is evidently made up of a certain definite number N of these atoms.

Yet the weight N.F of these atoms is never quite equal to the total weight q of substance used, because it is practically impossible to obtain any substance in a state of absolute chemical purity. Let Y represent the totality of foreign matter, then we shall have

$$q = NF + Y \qquad (1)$$

The very small ratio

$$y = \frac{Y}{NF} \tag{2}$$

will be a constant, very nearly, for the same larger mass of substance used as stock, provided that great care be taken in its preparation and keeping; otherwise y may vary from one experiment to the next. It certainly varies from one lot of material to another.

By the aid of this ratio y we can transform (1) into

$$q = NF\,(1 + y) \tag{3}$$

which will be found much more convenient for calculation.

The compound DF obtained by synthesis will not necessarily contaiu every atom N of the substance F; there may have been a loss during the chemical operation, and some of the atoms F may not form the compound DF, but some other, such as D_2F or DF_2.

If then N′ represents the number of atoms actually formed of the compound DF intended, we have necessarily

$$N' = N - n' \tag{4}$$

where n′ represents some real positive number. This gives us

$$\frac{N'}{N} = 1 - n \tag{5}$$

where

$$n = \frac{n'}{N} \tag{6}$$

represents the small ratio of the number of atoms F lost in the synthesis DF as such. That is, all N atoms of F may be present in the product p obtained by synthesis, but a number n′ thereof may not have combined in that manner.

For example, if F be Copper, and the process used oxidation; then of N atoms of Copper taken only N′ may have been oxidized to cupric oxide CuO, and n′ to cuprous oxide Cu_2O; accordingly

N′ will be less than N, or n′ is some definite number. In this case it is supposed that actually not an atom of copper was lost in the process of synthesis.*

But since it is impossible to oxidize copper — to retain the example just a minute longer under our eyes — without exposing it to a current of oxygen for some time, and as no oxygen is absolutely pure, and no apparatus absolutely tight, it is evident, that the product actually obtained will contain something more than the oxide, and that the percentage of *this foreign matter even will vary with the* TIME *consumed in the operation.*

From this general summary it is evident, that the total weight p of the product obtained by synthesis may be represented by

$$p = N' (D + F) + X \tag{7}$$

The small ratio

$$x = \frac{X}{N' (D + F)} \tag{8}$$

will not generally be a constant, but rather a function of the total AMOUNT *of F used and even of the* TIME *consumed in the synthesis.*

The amount X represents not only all accessory foreign matter, but also the uncombined or differently combined atoms of F not united with D to the particular compound D + F which it was intended to obtain.

Equation (7) may also be transformed to the expression more convenient for calculation

$$p = N' (D + F) (1 + x) \tag{9}$$

For every single determination made, that is, for every individual synthesis, the weights p and q have been ascertained experimentally; their quotient, or the *analytical ratio* of the determination will accordingly be represented by the following expression:

* See also the case of Richards, overlooking the formation of prosulphuric acid at the positive electrode, p 136.

$$a = \frac{p}{q} = \frac{N'(D + F) + X}{NF + Y} \tag{10}$$

or, by factoring, as shown above,

$$a = \frac{p}{q} = \frac{N'}{N} \cdot \frac{D + F}{F} \cdot \frac{1 + x}{1 + y} \tag{11}$$

Now, the variables x and y are very small quantities in comparison to unity, in all good determinations. Consequently, their products and higher powers are entirely insignificant, in comparison to themselves and to ordinary quantities. Thus, if they were only 2 thousandths each, their square would be 4 millionths only, and would be without influence on the third and fourth place of decimals. Hence

$$\frac{1 + x}{1 + y} = 1 + x - y \tag{12}$$

for the product $(1 + y)(1 + x - y)$ gives $1 + x$ and the insignificant quantity $xy - y^2$. We have also

$$(1 + x)(1 + y) = 1 + x + y \tag{13}$$

because the product xy is of no influence in comparison to x or y. That is:

Multiplication is effected by addition, division by subtraction, of the minute quantities x and y modifying the unit.

Accordingly (11) may be written:

$$a = \frac{p}{q} = \frac{N'}{N} \cdot \frac{D + F}{F}(1 + x - y) \tag{14}$$

By utilizing (5) this analytical ratio is reduced to

$$a = \frac{D + F}{F}(1 + x - y - n) \tag{15}$$

Now, since D and F represent the *true atomic weights*, the fraction

$$\frac{D + F}{F} = R \tag{16}$$

is the *true atomic ratio*, which we represent by the letter R.

This ratio must not be confounded with the *common* atomic ratio r obtained from the *common* atomic weights, and which was used in Part First.

The following is therefore the simplest expression of the *analytical ratio*:

$$a = \frac{p}{q} = R\,(1 + x - y - n) \qquad (17)$$

By the simple mathematical principle explained above, we can solve (17) directly for R:

$$R = a\,(1 - x + y + n) \qquad (18)$$

These two equations (17) and (18) constitute the ground work of the determinations of the *true* atomic weights.

We have purposely refrained to take note of the *errors of weighing*, because they can now be reduced to almost insignificant quantities, and are anyway quite familiar to all chemists. We have also assumed p and q to be absolute weights, or that the direct weighings have been corrected for buoyancy. In case this has not been done, the corresponding two minute quantities would have to be added in the parentheses (17) and (18).

We will now proceed to the general discussion of these fundamental equations.

A. THE ANALYTICAL RATIO.

The expression for a given in equation (17) shows plainly that *the analytical ratio is not a constant* but varies with the minute ratios x, y, n; for the true atomic ratio R is, by theory, a constant.

All determinations of precission confirm this law. We have seen that there is not a single series of determinations made by *Stas* in which the analytical ratio is rigourously constant. While empirically this variation has shocked the Stasians, it may, theoretically, be looked upon as a evidence of the remarkable

accuracy of his work, though neither Stas himself, nor the Stasians of to-day, have studied the general principles of science sufficiently to understand the causes of this variation.—See the curves on Plates I and II, and pp. 77–82 supra.

The precise form of this variation we will study in a subsequent section, E.

B. THE MEAN AND THE LIMIT.

All chemists have thus far conformed to the practice of Berzelius in the calculation of the atomic weights. They have taken the analytical ratio as a measure of the atomic ratio, that is

$$R = a \tag{19}$$

Hence, for a number of determinations, the mean of the individual values a was taken as the most probable value of the atomic ratio, which then gives, by (16), the atomic weight D, that of F being known.

This practice was sufficiently exact in the days of Berzelius, but cannot be continued when determinations of precision are really at hand.

Equation (18) explains the fallacy of the practice of modern chemists expressed in the erroneous equation (19). For the minute quantities x and n are certainly *not* constant, though y for the same material may be nearly so. Hence the ratio

$$\frac{R}{a} = 1 - x + y + n \tag{20}$$

necessarily differs from unity and *is variable*, being either slightly above or below unity. For example, for fused silver nitrate, this ratio is respectively 41, 46, 39, 40, 24 hundred-thousandths below unity in the five cases given at the bottom of page 83.

It makes no difference how many individual determinations of the analytical ratio a be made in any series; the mean of the right side (20) can never be equal to unity, but will remain throughout each individual series of precision either above or below unity.

All chemists ought to understand the impossibility of determining the true weight of a new coin by the weighing of any number of worn coins; since every one is light in weight, their mean will necessarily also be below the true weight.

C. THE TRUE ATOMIC WEIGHT IS A LIMIT.

But suppose we were to take the weight of these coins and also note the year in which they were struck. Suppose we were to take the mean weight for the coins of each year separately. If the number of coins examined were large enough, these means, when plotted as ordinates over the years as abscissae would determine a fairly regular curve, lowest for the oldest coins, gradually rising towards a *limit* which they would not quite reach. That higher limit would evidently be the true mean weight of the new coin. Such a method of procedure possesses the characteristics of a *Limit Method.*

By such a method the true atomic weight can be determined. For suppose that we carry out determinations under varying conditions, and plot the results according to the amount of matter taken as abscissae, and draw a separate curve for each set of minute quantities x, y, n; then the curves of the analytical ratios will approach the value R as the minute ratios x, y, n approach zero. That is mathematically expressed by the equation

$$R = \lim. a \qquad (21)$$

which reads: *the true atomic ratio is the LIMIT to which the analytical ratios approach as the disturbing quantities x, y, n are gradually approaching zero.* Contrast this with the wrong equation (19) used by chemists thus far.

When Dumas substituted the diamond for all other forms of carbon, he practically reduced y to zero; hence his results represented a wonderful progress, and the accuracy of his work has not yet been surpassed. Again, when he kept the oxygen gas in a gasometer filled with lime-water, he diminished x; the pro-

duct of combustion passing over red hot copper oxide secures every particle of carbon to reach the absorption bulb fully saturated with oxygen, so that also n is brought close to zero.

Hence it is that the mean of his five determinations gave the analytical ratio $a = 3.6663$, while the true atomic ratio is $R = 3.6666$.....Accordingly the atomic and analytical ratios are almost equal, for

$$\frac{R}{a} = 1.000\ 08$$

differs by less than one ten thousandth from unity. See p. 21.

The chemists of the old school have been particularly careful to purify the substance used for their determinations, say by repeated re-crystallizations. In such cases, the purer substance for which y is nearer zero—will give, other things being equal, an analytical ratio which approaches nearer to the atomic ratio. *Such determinations should have the preference*, and should *not* be combined to a general mean with determinations made on substances that were less pure. This self-evident principle is generally disregarded by modern chemists who thus present us an olla potrida—which is as objectionable as the Consommé Pelouze.

But this method of approaching the limit by *qualitative* processes is very laborious, and requires a multitude of determinations as well as extreme circumspection. I have therefore devised a *quantitative* limit method, by means of which one single *series* of determinations will furnish the true atomic ratio.

D. THE LIMIT METHOD.

My LIMIT METHOD* requires the execution of a true SERIES of determinations, all made under exactly the same conditions with exactly the same materials, and differing only in the *amount*

* Comptes Rendus, T. 116, p. 753; 1893.

of the independent taken; and this amount should vary gradually between the two extremes determined by the possibility of ready handling and exact determination. As to chemical reactions, only the simplest and most direct should be chosen, parting from and leading to perfectly definite physical and chemical entities, sufficiently permanent to permit accurate weighing. This excludes all volumetric processes. Finally, the reaction must be completed in the shortest possible time; for time enters in x as a disturbing element.

If such a series of determinations A, B, C, D, ... is plotted (Fig. 7) over the weight q or w as abscissa, and the ana-

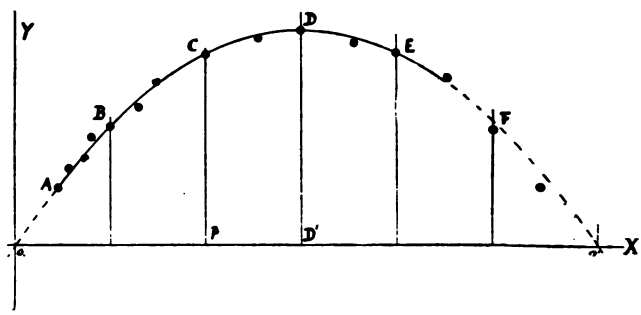


Fig. 7.

lytical ratio a as ordinate, the latter will determine a *parabolic trajectory*, which has its convexity either turned up or down, and accordingly exhibits either a *maximum* or a *minimum*.

Now, when a sufficient number of points A, B, C, ... have been determined in this trajectory by a corresponding number of determinations for values of q = w, properly varying between the limits depending on the practical conditions of the chemical process, the curve most closely passing through all points so determined can be drawn, and continued so as to cut the ordinate axis; the ordinate so cut off at o will represent the true *atomic ratio* R.

For the disturbing quantities x, y, n depend on the amount

of material taken; the smaller the amount of matter used, the nearer we approach towards the ideal case of the single atoms D and F. Accordingly, the limit $w = q = o$ will also involve $x = y = n = o$, and these give $a = R$. The case presents *not* an indefinite ratio %, but the tangent to the curve determined shows the direction and will cut the ordinate so much the more accurately, as the series has been carried on nearer to $w = o$.

Through the point o determined by the curve, draw the horizontal oX as the new axis of abscissae w, then the *analytical excess* e will be the new ordinates for the trajectory. Thus, for the point C of the curve, $oP = w$, is the abscissa or weight q used, and $CP = e$ the *analytical excess*, that is the excess of the analytical ratio over the atomic ratio represented at o. Such are the curves on Plates I and II.

E. EQUATION OF THE TRAJECTORY.

Since these curves (see Plates I and II) are nearly symmetrical and greatly resemble the common parabola, they will, as a first and generally sufficient approximation, be expressible by the equation of two terms

$$e = kw - k'w^2 \tag{22}$$

where k and k′ are constants.

To determine these constants let u be the range oo′ and h the maximal height (or depression) DD′ of the curve, considered as a parabola. Then (22) gives, for $e = o$, the range $u = w$

$$u = \frac{k}{k'} \tag{23}$$

Since the greatest elevation (or depression) h corresponds to half the range, we obtain $e = h$ by substituting $w = \frac{1}{2}u$ in (22), giving

$$h = \frac{k^2}{4k'} \tag{24}$$

Hence if we have experimentally determined the curve, and from it, by direct measurement, have taken the values of h and $\frac{1}{2}$u for the highest (or lowest) point, we can calculate the constants k and k′ of the trajectory (Fig. 7) by

$$k = \frac{4h}{u} \qquad k' = \frac{k}{u} = \frac{4h}{u^2} \tag{25}$$

It is also interesting to determine the *angle of elevation* θ' under which the highest (or lowest) point appears when seen from the origin

$$\operatorname{tg} \theta' = \frac{2h}{u} \tag{26}$$

The angle θ under which the trajectory cuts the horizontal axis is evidently determined by

$$\operatorname{tg} \theta = k = \frac{4h}{u} \tag{27}$$

Consequently we have, the angles being very small,

$$\theta = 2\theta' \tag{28}$$

EXAMPLE. The curve representing the syntheses of silver sulphide (Plate II) shows the maximum 43 (in the 5th place) for 178 grammes of silver.

That is, h = 0.000 43 and u = 356 grammes.

Consequently, (25) gives the constants of the parabolic trajectory

$$k = 0.000\ 004\ 83$$
$$k' = 0.000\ 000\ 01$$

and θ is one second of arc, θ' half a second of arc. The equation of this trajectory is accordingly

$$\begin{aligned} e &= 0.000\ 004\ 83\ w \\ &\quad - 0.000\ 000\ 01\ w^2 \end{aligned} \tag{29}$$

or approximately

$$e = 0.005 \frac{w}{1000} - 0.01 \left(\frac{w}{1000}\right)^2 \tag{30}$$

which, if we put $w = 1000\, w_1$ assumes the convenient form of

$$e = \frac{5w_1}{1000} - \frac{w_1{}^2}{100} \tag{31}$$

The minuteness of the values of the coefficients gives a correct idea of the real form of the curves, which in our drawings are necessarily greatly distorted.

It is quite apparent that the quantities here considered are exceedingly minute in comparison to the weights involved. Accordingly, the coefficients k and k′ are frequently the first only a few millionths, the latter even only a few hundred millionths, while the true trajectory differs from a straight line by only a few seconds of arc.

These facts mark the intrinsic difficulties of the problem here under consideration. *They also testify to that excellency of the work of Stas, which his professed admirers have never properly comprehended.* The work of Dumas on water was equally exact and preceded that of Stas.

It will be understood that for every single series of analytical determinations such a trajectory is obtained. Provided the chemical reaction employed is the same, all these trajectories must cut the ordinate axis in the same point.

In the next chapter we shall show in what manner this limit method can be most readily applied.

F. LIMIT METHOD IN GENERAL.

It would seem that chemists of to-day are not acquainted with the important position which *limit methods* have occupied in the progress of science. They have been making desperate efforts to determine the atomic weights of the elements directly, and have applied the clumsy and irrational method of means to the results of their experiments. They do not seem to understand that the final mean must necessarily be too low, if all the individual determinations are too low.

The mean values of the determinations of Stas come no nearer the true atomic weights, than the "mean man" of his eminent colleague of the Brussel's Academy of Sciences approaches the

proportions of the true man. "L'homme moyen" of Quetelet is a caricature of beauty, and the mean atomic weight of Stas is a libel on the wonderful laws of proportion imprinted on matter. In its more general aspects the same empiricism of the "mean" is clouding all branches of modern science, and having become the fashionable philosophy of the last half of this century, is leaving its depressing and debasing marks in almost every sphere of human action.

In the highest branch of scientific chemistry the method of means has well nigh produced chaos while filling the chemists with proud ideas of a high degree of precision and accuracy that has no existence except in their own imagination.

On the contrary, the periods of greatest development in the history of the exact sciences have been marked by the introduction of limit methods.

Dynamics rests upon the law of inertia; but this could never have been established as a "mean" but is accepted as a "limit." In proportion as we remove resistances to motion, this motion continues; and we infer that the motion will continue indefinitely without change, if the resistances become absolutely zero.

The law of uniformly accelerated motion involved the infinitesimal time limit, during which any motion may be taken as uniform. Galilei had grasped this idea very clearly.

In fact, the great development of higher mathematics in the days of Cartesius, Cavalieri, culminating with Leibnitz and Newton, is mainly due to the introduction of a limit method. If Δ represent finite differences and d the differential, we have, as the most general principle of calculus

$$\frac{dy}{dx} = \lim. \frac{\Delta y}{\Delta x} \tag{34}$$

Now, the mean of the finite differences Δ will never give the differential, nor their ratio the differential quotient. Or, if it be easier understood, the mean of a series of secants passing through

a given point in a curve will never give the tangent to that point; for that tangent is the *limit* of these secants.

It must suffice to specify these few instances; modern mathematical science is full of striking examples, in analysis, in geometry, and in mechanics, as a necessary consequence of the origin of these sciences.

But the limit methods are not themselves of modern origin. When the ancient geometricians wished to determine the length of the circumference or the total area of a circle for a given diameter, they utterly failed while trying methods of ordinary, direct procedure; they succeeded when applying a limit method.

They knew that the inscribed regular hexagon has a perimeter of exactly six radii. They had, by ordinary linear geometry, determined the length of the side of any polygon of exactly double the number of sides. Consequently they determined the perimeter of the regular 12-sided polygon to be 6.211 656.

In the same manner they determined the perimeter of the regular polygon of double the number of sides, that is of 24, 48, 96, 192 ..... sides. The results of such a calculation is given below, correct to six places.

	Perimeter of Regular Polygons.	
No. of Sides.	Inscribed.	Circumscribed.
6	6.000 000	6.928 203
12	.211 656	.430 782
24	.265 257	.319 320
48	.278 700	.292 173
96	.282 064	.285 429
192	.282 906	.283 746
384	.283 114	.283 324
768	167	220
1536	180	194
3072	184	188
Infinite.	185	185

Now, plot these values, say by starting with the inscribed polygon of 96 sides, taking a convenient length as abscissa to represent the corresponding angle; half that length will then be the place for the ordinate for the polygon of 192 sides. See

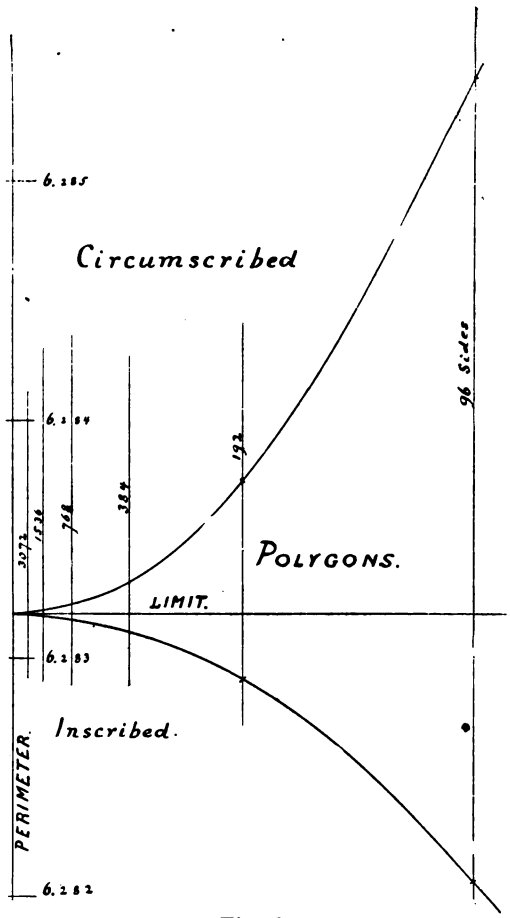


Fig. 8.

Fig. 8. For each abscissa erect the corresponding ordinate—say in *excess* of 6.282.

By now joining the points so determined a regular *curve* re-

sults, which produced cuts the initial ordinate at a point determining the length of the perimeter of a regular polygon of infinitely many sides, i. e. the *limit* of all inscribed polygons, which we call the circle.

This is done practically in the most accurate manner by drawing the tangent to this curve. It will be only one unit in the sixth place in excess of that for the 3072-sided polygon. Hence the circumference, to the sixth place, is 6.283 185 if the radius is one.

Since now the circumference is commonly represented by 2π, it follows that the ratio of circumference to diameter of any circle is

$$\pi = 3.141\ 592 \ldots$$

This is probably the oldest application of a limit method. It can be greatly perfected by considering the ordinates measured from the tangent, which are seen to diminish to one-fourth at each upward step. For the 96-sided this difference is 1121; for the next higher ones it is 279, 71, 18, 5, and finally 1. Now if 1121 is five times reduced to a fourth, it is reduced to one 1024th; which gives 1.1 as the value to be added to the length of the 3072-sided polygon, so that the figure given is exact to the sixth place. This curve is a parabola.

It is evident that this determination of the circumference corresponds exactly to our determination of the atomic ratio; the method used is the *limit method*, the foremost method yet devised by the human mind for the determination of those quantities which it seems impossible to determine directly.

It hardly need be added that starting with the circumscribed hexagon, the same limit method gives a higher limit for the length of the circumference. Our diagram, Figure 8, represents also this series of approximations by the corresponding curve. The tangent is common to both parabolæ. The true value always is between these two limits. Hence, as these limits approach,

the value of the quantity to be determined becomes known with a high degree of precision.

The corresponding higher and lower limit also can be used in chemistry. Thus the atomic weight of oxygen results from potassium chlorate too low, while from silver chlorate it is obtained too high. The two limit curves intersect in $O = 16$ exactly. Compare Fig. 4, Plate II.

It may seem a little out of place to introduce portions of elementary geometry into our work on the determinations of the true value of the atomic weights, but as it appears that some chemists in high position have no knowledge of the important place which limit methods occupy in the history of science, the pages devoted to this topic will serve a useful purpose.

I may be permitted to add that this exposition is entirely new in form. I believe it is also new as a theorem that these limit cnrves are parabolæ.

CHAPTER II.

PRACTICAL FORM

OF THE

LIMIT METHOD.

If we could separately handle the two individual atoms, it would be easy to determine their atomic weight (p. 2); we would first weigh the one single atom, then the combination of the two. But this being impossible, we have to deal with *masses* directly, and can only obtain the true atomic weights as a *limit*.

If the earth were the only planet circling around the sun, astronomers would have an easy time of it, for the earth's orbit would be an ellipsis, *exactly*. But since there are other planets in our system, the earth does at no time describe that ellipsis exactly; it is constantly more or less disturbed in that orbit, by the other planets.

But these other planets being very small in comparison to the central body, the sun — even Jupiter having less than the thousandth part of the mass of the sun — these disturbances are comparatively small in amount. Astronomers (not those of the Observatory, p. 57, foot note), have solved the problem of perturbations, the problem of the three bodies, not by any direct process, which is manifestly impossible, but by a limit method. They take the elements of the earth's orbit, determined on the supposition that the earth is the only planet revolving about the

sun; they then consider the perturbations produced by the other planets as causing minute variations of these elements, which thus are no longer real constants, but *constants subject to very small variations.* This is the famous method of the *Variation of the arbitrary constants of Lagrange.**

In Chemistry, the disturbing effect of other kinds of atoms than the two involved in the process may be determined by the same general method of the variation of the constants; for here the disturbing influences can experimentally be *made* very minute by keeping away as much as possible all other or foreign matter. We then must consider the *atomic weight* D to be determined as a slightly variable constant; that is, if D represent its true value, we shall find an atomic weight equal to D + d under the conditions of our chemical process. Now the variable quantity represented by d is necessarily very small in comparison to the constant D; that is, the ratio

$$\frac{d}{D} = \delta \tag{35}$$

is very small. We shall call this ratio δ the CHEMICAL PERTURBATION. These quantities are in all cases sufficiently small to allow the use of the method of calculation peculiar to minute quantities, in connection with comparatively very large ones; see p. 143.

If we now revert to the original and complete expression of the analytical ratio, namely (p. 143)

$$a = \frac{p}{q} = \frac{N'(F + D) + X}{NF + Y} \tag{36}$$

* C. RAMUS. Differential og Integral Regning, Kjöbenhavn, 1844, p. 116, 147.
— Analytisk Mechanic, 1852, p. 284, etc.

JAMES C. WATSON. Theoretical Astronomy, Philadelphia, 1868, p. 42 and p. 426 seq.

In our applications we need only the very rudiments of this most fertile method. If we ever publish the Principles of Atom Mechanics, we shall need more of this method.

we see that the introduction of the minute variable d can take the place of all the other variables, and reduce the above equation to

$$a = \frac{p}{q} = \frac{F + D + d}{F} \tag{37}$$

This equation is entirely general; D and F representing the *true* atomic weights.

But we can go one step further. Since the true atomic weights, as a matter of fact, differ but very slightly from the common atomic weights (p. 5) the above equation (37) will be equally true if D be taken as the *common* atomic weight of the element in question; in that case d will become the *departure*, and δ we will continue to call the *chemical perturbation* or departure for a unit of weight.

In this case

$$\frac{F + D}{F} = r \tag{38}$$

is the *common* atomic ratio, the same we have been making use of in Part I.

Accordingly, (37) gives us

$$a = r + \frac{d}{F} \tag{39}$$

or, since the *analytical excess* is

$$e = a - r \tag{40}$$

we find the *departure* to be

$$d = Fe \tag{41}$$

and the *chemical perturbation*

$$\delta = \frac{F}{D} \cdot e \tag{42}$$

The departure of the atomic weight from its common value D *is obtained by multiplying the analytical excess* e *by the atomic weight* F *that has been combined with the element* D.

The minute analytical excess e, being multiplied by the

atomic weight F will give quite appreciable values of the departure d. See pp. 79—80, supra.

Since in Part I, we have found as a chemical fact, that the analytical excess is variable, it follows that *the departure is variable, and consequently the atomic weight* D + d *is variable,* according to all the determinations of Stas and Dumas without exception. And since the trajectory e is approximately parabolic we can give the general equation of the atomic weight,* by means of equation (22).

But since for w = o, d vanishes, it follows that the *common* atomic weight D is the *true* atomic weight, provided the formula (41) is a true representation of the facts observed, or more generally, *provided that the trajectory passes through the origin.*

Now, since the analytical excess varies regularly with the amount of substance used in the determination, and approximately as the ordinate of a parabolic curve passing like the trajectory of a projectile from the origin, and since the departure is directly proportional to this analytical excess (equat. 41), it follows that *the atomic weight of an element results* NOT *as a constant from these analyses, but varies regularly and continuously with the weight of substance used for its determination, very nearly as the ordinate of the trajectory of a projectile.*

The departure d we will generally express in thousandths (or units of third place). It is the small variation to be added to (or subtracted from) the common atomic weight to give the particular value of that atomic weight resulting from the individual experiment specified.

The following tables give the values of the departures mainly from Stas' analyses. In the first table, we have put together all departures determined by means of pure silver, the atomic weight of which has been (temporarily) taken at 108 exactly. Accord-

* The same is equally true for the chemical perturbation.

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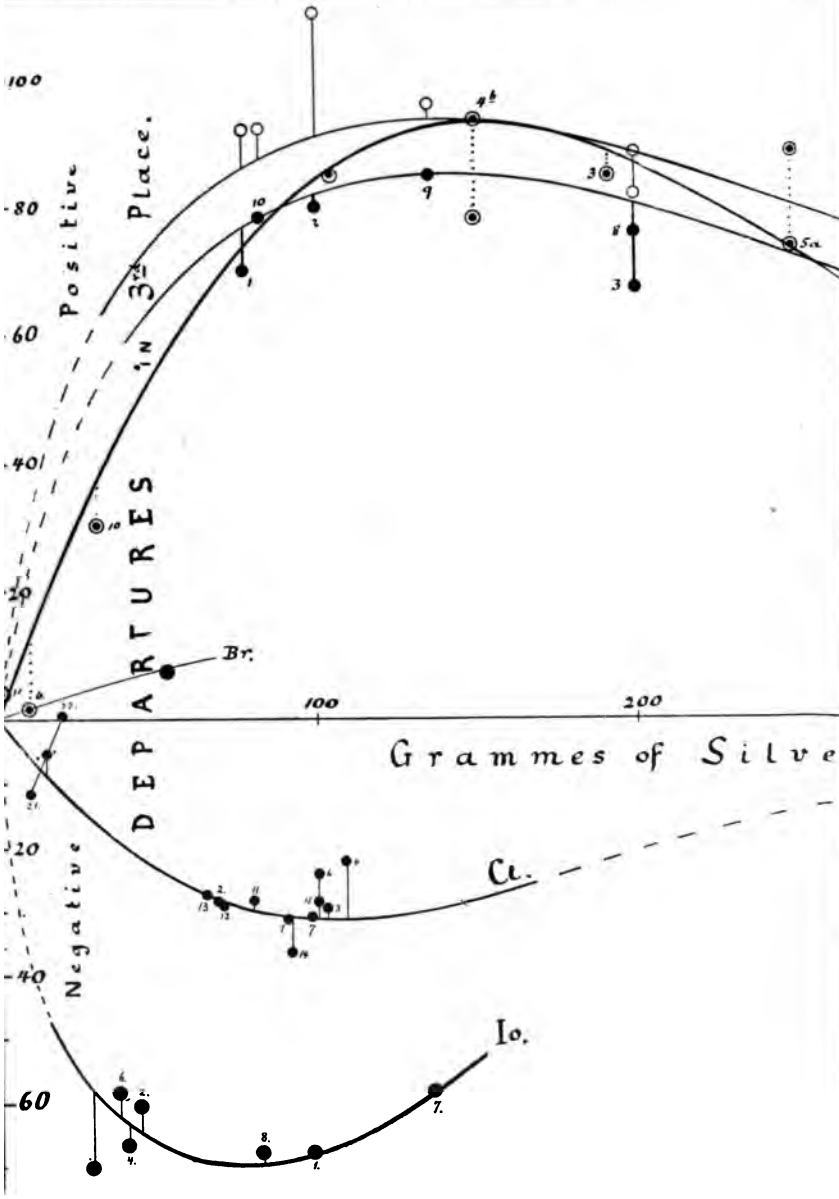
PLATE III.


DEPARTURES IN 3rd Place.
Positive
Negative
Br.
Cl.
Io.
100
200
Grammes of Silve
80
60
40
20
-20
-40
-60

-eparture e for the atomic weight of another element ordingto (41)

$$d = 108.\ e$$

analytical excess determined in the preceding part. e relation employed p. 79.) In the case of sulphide, of sulphur is combined with two atoms of silver, the is evidently 216 e.

second table, the determinations made with pure lead tabulated in the same manner. Lead nitrate contain- atoms of nitrogen, we have necessarily 2 d = Pb e or 5 e, taking Pb = 207 temporarily.

xperimental data are not repeated in these tables, but lily be looked up by the references given.

[TABLE 19.]

TABLE OF DEPARTURES (3D PLACE).

METAL: SILVER.

NITROGEN. SYNTHESIS SILVER NITRATE.

Table 6, p. 81.

	Departure.				Departure.	
Silver.	Dried.	Fused.	No.	Silver.	Dried.	Fused.
77	92	70	6	405	69	60
100	111	80	7	200	57	46
200	82	76	8	200	88	67
300	75	69	9	136	96	85
300	77	68	10	82	95	78
			6,	corr.	50	41

ry, Table p. 83.

77	92	70	4, 5	300	76	69
150	97	78	6	405	50	41
200	87	67				

GNAC, Table 7, p 88.

69	28	4	70	— 3	
58	— 7	5	200	43	
66	28	mean,	1—4	11	

SULPHUR. REDUCTION OF SILVER SULPHATE.

STAS, p. 95.			H. STRUVE, p. 96.		
Series.	Sulphate.	Depart.	No.	Sulphate.	Depart.
III	60	117	1	5	—59
I	66	140	2	6	—54
II	80	113	3	9	14
			4	12	72
			5	9	86
			6	9	—28
			Mean,		5

SULPHUR. SYNTHESIS OF SULPHIDE. Table 12, p. 98.

STAS.			DUMAS.		
No.	Silver.	Depart.	No.	Silver.	Depart.
1	59	81.4	6	10	11.2
2	105	84.6	7	10	— 8.2
3	192	84.8	8	31	50.1
4*a*	150	78.2	9	31	19.8
b	150	92.9	10	31	20.0
5*a*	249	73.6	COOKE.		
b	249	88.1	11	1	—10.3
			12	1	18.4

CHLORINE. SYNTHESIS OF CHLORIDE. Table 13, p. 103.

STAS.			MARIGNAC.		
1	91	—31.4	11	80	—28.4
2	69	—28.7	12	70	—29.4
3	102	—29.5	13	65	—27.5
4	109	—22.3	14	92	—36.5
5	400	—26.4	15	100	—28.5
6	100	—24.0	DUMAS.		
7	98	—30.9	21	10	11.7
			22	20	— 0.9

BROMINE. SYNTHESIS OF SILVER BROMIDE. Table 14, p. 106.

No.	Silver.	Depart.	No.	Silver.	Depart.
1	53	8.3	11	25	— 2.2
2	51	4.5	12	20	—19.8
3	55	5.4	13	15	— 8.0
4	56	3.7	Mean,	20	—10.0
5	48	10.5			
Mean,	53	7.4			

IODINE. SYNTHESIS OF SILVER IODIDE. Table 15, p. 108.

No.	Silver.	Depart.	No.	Silver.	Depart.
1	98	—67.9	5	24	.....
2	44	—60.7	6	38	—58.6
3	28	—70.7	7	136	—58.4
4	40	—67.0	8	82	—68.2

[TABLE 20.]

TABLE OF DEPARTURES. 3D PLACE.

METAL: LEAD.

NITROGEN. SYNTHESIS OF LEAD NITRATE. Table 8, p. 91.

No.	Lead.	Depart.	No.	Lead.	Depart.
1	103	72.9	6	124	72.7
2	141	74.5	7	100	69.0
3	110	85.5	8	200	63.1
4	142	74.0	9	250	57.9
5*a*	149	41.8	10	250	64.2
b	.....	66.9			
Summary, p. 92.					
1, 7	101	71.7	8	200	63.1
6	124	72.7	9, 10	250	61.0
2, 4	142	74.2			

SULPHUR. CONVERSION OF NITRATE TO SULPHATE. Table 9, p. 93.

4	142	138.7	8	200	113.9
5	149	103.5	9	250	91.1
7	100	86.9	10	250	95.2
Summary, p. 93.					
7	100	86.9	8	200	113.9
4, 5	145	121.1	9, 10	250	96.1

EXAMPLE: NITROGEN.

In order to more readily understand the entire question, we will reprint in full the summary above given for the departures of Nitrogen as resulting from the famous syntheses of silver nitrate made by Stas. Since the common atomic weight of nitrogen is 14, and since the departures are given in the third place, the departure 78 indicates that the corresponding synthesis gives as atomic weight of nitrogen 14 units and 78 thousandths, that is the value 14.078.—It being understood that Ag = 108 and O = 16.

STAS' SYNTHESIS OF SILVER NITRATE.

No.	Silver, Grammes.	Atomic Weight from Nitrate Dried.	Fused.
1	77	14.092	14.070
2, 3	150	14.097	14.078
8	200	14.087	14.067
4, 5	300	14.076	14.069
6	405	14.050	14.049

The last value has been corrected by reducing the barometric pressure form 54 inches to 30 inches; see p. 83.

This small table shows the fact of the very considerable variation of the atomic weights resulting from the best analyses made.

GRAPHIC REPRESENTATION OF DEPARTURES.

The importance of the subject, and the unexpected nature of the results, make it advisable to represent the data of the first table (for Silver) graphically. We have done so in Fig. 9, Pl. III, which accordingly represents the departures of the atomic weights of Nitrogen, Sulphur, Chlorine, Bromine and Iodine from their common values 14, 32, 35.5, 80 and 127. The weight of the silver used in each experiment, has been taken as abscissa. The departure resulting (from the analytical excess) has been repre-

sented as ordinate, the scale used being very large, the numbers representing units in the third place of the atomic weight.

Of course, these curves represent the atomic weights of these elements resulting from their silver compounds when using the amount of silver specified by the abscissa. Now since in the original drawing, 10 in the third place were represented by an inch, the *unit* of the atomic weight corresponding is represented by 100 inches or $8\frac{1}{3}$ feet (2.5 meters); that is the length which the ordinates must be produced downward below the horizontal base of the drawing, to represent the atomic weight of hydrogen. The atomic weight of nitrogen therefore is represented in my original drawing by a length of $116\frac{2}{3}$ feet (35 meters) *plus* the departure represented in the curve above that horizontal. In the same way, the atomic weight of chlorine is represented by a line 306 feet (100 meters) long *minus* the departure represented in the original drawing.

Since the printed cut is reduced to one-third the scale of my drawing, it follows that the unit of atomic weights, H=1, is represented by almost 3 feet (83 cm); that the atomic weight of nitrogen is represented by continuing the ordinates on the printed figure almost 39 feet (12 meters) downward, while for the atomic weight of chlorine they have to be continued almost 102 feet (33 meters) downwards, in round numbers.

It is very important to keep in mind these true magnitudes in order not to be mislead by the apparently large departures represented in the figure. The case is exactly the same as in the representation of the elevation of a continent or in astronomical diagrams; the abscissa is represented on a very small scale in comparison to that used for the ordinates. Compare p. 151.

It would, of course, be absurd to suppose that the atoms of nitrogen vary in weight according as they are constituents of silver nitrate made form 100 grammes or 400 grammes of silver, or according as the silver nitrate has been dried or fused. *The*

differences in atomic weights resulting from the different experiments of Stas simply indicate and measure the chemical perturbations remaining beyond the control of the experimenter. They are in the nature of residual errors—but such as show a definite functional variation, and thus manifest a force overlooked—in this case, the chemical perturbation.

We also see that in all cases, these departures of the atomic weight determined are a maximum for a certain absolute weight of the metal used for their determination, diminishing slowly for increasing weights, and generally much more rapidly for diminishing weights.—These curves necessarily correspond to those of Plates I and II. See equation 41.

Now, as the weight of the matter employed diminishes we approach the ideal determination of weighing a single atom. The *true* atomic weight is therefore that value, to which the curve of departures approaches as the weight of material used approaches this vanishing point or zero. That is, the true atomic weight of an element corresponds to the lower limit of the analytical excess and ratio, as expressed by our formula (21).

$$r = \lim. a \qquad (43)$$

GENERAL CONCLUSIONS.

To certain professedly prominent chemists who seem to have long ago lost all power of exact chemical and mechanical reasoning by the habit of constructing elegant structural formulae of complex organic compounds, our limit method and its results will naturally appear as a new *theory*—for they never seem to have troubled their minds very much with the study of the methods of the exact sciences recorded in its history. We shall not undertake the hopeless task of supplementing their elementary training (Foot-note p. 84).

But to the young chemists, who are still thirsting for knowledge and have not yet put goggles on their mind's eyes; to all older chemists, who have not entirely devoted themselves

to the study of the tar-derivatives, and to all scientists who have thoroughly mastered the rudiments of mathematical knowledge and methods: the diagram (Fig. 9), representing the direct results of the most accurate chemical analyses ever made, does show

I, that the atomic weights, determined experimentally, represent variable quantities and not constants;

II, that the means of these determinations are taken in violation of the principles of science, and do not represent any physical quantity whatever;

III, that the individual values determined vary according to a definite law, approaching a definite limit as the quantity of matter operated upon approaches zero; and that this limit gives the true atomic weights on which chemical science is to be built.

HISTORIC RETROSPECT.

If we throw a projectile by arm or gun under a definite angle, we do not expect it to describe a straight line, for we know that All Nature continues to act upon that projectile after it has left us; gravitation converts the straight line into GALILEI's parabolic orbit, which, by the resistance of the air, is further modified into the ballistic curve proper, with its final vertical asymptote which the projectile descends with uniform velocity.—The trajectory of atomic departures evidently resembles the trajectory of a projectile.

If we observe the great system of the sun, we see, with COPERNICUS, the planets all revolving around the central light; upon closer inspection we learn, with KEPLER, that these orbits are not exactly circles, but ellipses of small excentricities, the sun being the common focus of all; with NEWTON, we next see how these motions are produced, but also notice the harmony partly destroyed by apparently irregular and even threatening displacements and changes in velocity, called perturbations; but with LAPLACE we learn, that these perturbations themselves form a

new harmony of a higher order, and finally we become able, with LEVERRIER, to recognize the unseen worlds beyond in the slow tremors of perturbation of the furthermost planet so-far observed.

The general course of scientific research is the same in the different forms under which the same nature appears to man. The course of the science of the chemical atom will therefore resemble that of her elder sister of the cosmical atoms.

Chemists have, with LAVOISIER, established the fixed specific, individuals of matter, the elements. BERZELIUS has experimentally demontrated the laws of DALTON on the fixed, simple multiple proportions in which these elements combine. DUMAS has determined two of the most important atomic weights with precision, and made it probable that another GREAT ENGLISH THOUGHT, the so-called Hypothesis of PROUT, slightly modified, is essentially conform to nature.

The empiric system of STAS now swept all before it, while most chemists of one of the leading nations retired to a tar barrel,* and after taking a look at the results of Stas through the bung hole, declared the hypothesis of a common multiple in the atomic weights of the elements a chimera.

If astronomy had been cursed with such a period of empiricism, as has befallen chemistry since 1860, the laws of Kepler would have been blotted out as chimeras, and for universal gravitation there would have been no foothold; cycles, more refined, but of the same general character as those of the Egyptians and Chaldeans, would be used where now the theory of gravitation has developed into the grandest science, the glory of mathematical reasoning.

In showing that Stas and his school did not understand their own experimental data, and that, therefore, they were not com-

* Not entirely for pleasure, but very much for profit. They now boastfully insist that the chemists of the other nations "got left." With all due respect for the scientific results incidentally obtained, I am reminded of Schiller's excellent definition of Science:

Einem ist sie die hohe, himmlische Göttin, dem Andern
Eine tüchtige Kuh, die ihn mit Butter versorgt.

petent to draw the conclusions they did, we have cleared the field for deeper research. We have next shown that the best determinations made in the laboratory by the best analysts, including Stas himself, cannot remove the perturbations of surrounding nature; *that it therefore is as impossible to obtain constant values for atomic weights with increasing amounts of matter, as it is to project a body in a truly horizontal line with increasing velocity of projection;* that finally the conflicting individual determinations have their common limit for a vanishing amount of matter in the true atomic weights of the elements.

THESE ATOMIC WEIGHTS ARE ABSOLUTE AND FIXED BY NATURE, not by some superficial government calculator, invited by some society of friends to furnish them, once a year, the atomic weight quotations from the stock board of the performing chemists. Empirics have, in these days of vaunted liberalism, finally reached the same state in science which they so roundly denounce when they recognize it in the Church about the time of the Reformation. It was just as proper and equally as comforting to the mind, unwilling to reason for itself, to accept the dictum of a Pope, as for chemists to take their constants of Nature from a department of our Paternalistic Government. I may be permitted to add, that those who relied on the Pope were no more likely to be mislead, than their present representatives.

In the third part we shall learn that THE TRUE ATOMIC WEIGHTS OF NATURE INDEED ARE EXACT MULTIPLES OF HALF THE ATOMIC WEIGHT OF HYDROGEN, and finally, that all elements are compounds of one single primitive substance, the PANTOGEN.

A HISTORIC PARALLEL.

In their very essence, the true atomic weights are physical *constants* of nature; for the atoms are the only physical units of the material world, if they exist at all.

Near the close of the year 1892, I began the long deferred publication of a series of NOTES in the COMPTES RENDUS of the

Academy of Sciences of Paris, showing by numbers and curves that the atomic weights resulting from the individual determinations of STAS are in no wise constants, but exhibit a marked regular variation as function of the amount of matter employed in the individual determinations.

In the present work the subject of these NOTES has been more fully developed, by presenting all the necessary details. The FACT stated is undeniable. The atomic weights resulting from Stas' determinations are not constants, but variable quantities. By arbitrarily selecting the amount of silver, we could obtain an indefinite number of systems of atomic weights from the determinations of Stas. This would certainly be more scientific than the fashionable habit of throwing away those determinations which do not agree with preconceived notions.

Now, does the history of science offer a parallel case, in which careful determinations of facts have proved the value of a natural constant to appear actually changing to a notable extent? If so, the historic parallel might prove useful to calm the minds of chemists that seem to have been disturbed by our preliminary representation of facts in the Comptes Rendus.

To my knowledge, the history of science furnishes only one such parallel case, namely the discovery, by Halley, of the secular variation in the motion of the moon. The astronomers of his day have, like the chemists of to-day, tried to deny the reality of the apparent paradox; but the eclipses observed by the Chaldeans, the Greeks, the Arabs and the Modern Astronomers establish the progressive variation in the time of revolution of the moon, exactly as the analyses of Dumas and of Stas have shown us the gradual variation in the atomic weight, dependent upon the amount of matter taken.

A century has elapsed since Laplace* traced the cause of

* LAPLACE, SYSTÈME DU MONDE. III. edition, Paris, 1808, pp. 222—225. This subject has since been developed by Adams, Cayley and Delaunay. The question of the exact constancy of the length of day has also been brought into this discussion especially by Delaunay.

the secular variation of the moon's motion to the slight variation of the excentricity of the earth's orbit. The cause of the variation in the values of the atomic weight we have shown to be due to chemical perturbation, the expression of minute impurities and deviations from perfect homogeneity. We have also shown how, by our limit method, we make ourselves completely independent of these minute pertnrbations and obtain the exact value of the true atomic weights of the elements.

It is interesting to notice that in the case of astronomy, depending for its facts upon observation, it has required twenty-five centuries of careful observation to recognize the existence of this secular variation, while in Chemistry, facts being obtainable at will by experiment, it was sufficient to increase the weight of silver used from one to two hundred and fifty grammes, in order to produce the variation of the atomic weight of sulphur so strikingly shown in our diagrams representing the experiments of Cooke, Dumas and Stas.

If our modern chemists, who insist on being recognized as leaders in our science, had devoted some of their time of study to those branches of the science of Nature which have attained a higher degree of development, than chemistry had reached in their school days, they would not have placed on the pages of the annals of chemistry so glaring confirmations of the truth of *Lichtenberg's* keen remark which for over a century has enjoyed perennial youth:

Wer nur Chemie versteht,
Versteht auch die nicht recht.

CHAPTER III.

A RATIONAL SYSTEM OF ATOMIC WEIGHTS.

We are now in the possession of a method by which a single series of determinations will give us the true atomic weight of a given element. We therefore must next unite the determinations for the different elements into one system, by the adoption of a proper STANDARD MATTER and a suitable UNIT OF VALUE. We can thereafter select the chemical processes and the proper order of succession and combination of the same, to secure the determination of the true atomic weights of all the elements.

Having seen to what enormous extent chemical perturbations modify the values of direct experiment, we cannot allow any indirect determinations nor any of the multiple linkings practiced in the system of Stas.

If we desire the atomic weight of chlorine, we must directly compare it with that of an element the atomic weight of which is known with precision, say silver; it will not do to obtain it by two processes, both of which are untrustworthy—such as the silver chloride reaction in the wet way and the potassium chlorate reaction in the dry or wet way—and fondly imagine that the process of mathematical elimination will remove any of the numerous chemical errors, or that the process of mathematical

elimination can give true values when the actual quantity eliminated from two equations is not identically the same in both.

These erroneous methods have become so ingrown into modern Chemistry, that we cannot often enough protest against them. I have already in an early Note in the Comptes Rendus (T. 116, p. 695; 1893) given considerable detail on this subject. I may, therefore, pass the same with the following simple illustration.

The determination of the true atomic weights of the different chemical elements may be compared to the determination of the principal points of a country by triangulation. Now, the first thing that is done is the establishment of fixed marks; all labor would be lost if the points themselves were not perfectly definite and fixed, so that they can be found again at any time.

But in the determination of the atomic weights, chemists have constantly changed their points of comparison, their standard values. In the *Note* referred to I have shown how the fact that the true atomic weights at best differ but slightly from the common whole numbers, could have been utilized by Chemists. We have, in the preceding chapter, fully developed that matter, and shown how the departures (écarts) are determined.

Again, the determination of the atomic weight of an element may be compared to the determination of the place of the ship on the ocean. Two methods are used; by means of the log and compass, and by observations of the sun, moon and stars. Now, during storms and in cloudy weather, the log is the only method available—but its results are known to be necessarily very unreliable. The first clearing of the sky is therefore taken advantage of for making an observation of the fixed or accurately known points of the heavens to obtain the ship's place with certainty and reasonable accuracy.

Now the former method in chemistry corresponds to the use of multiple proportions, none of which is known with accuracy,

while the latter corresponds to the use of simple and direct chemical reactions only and their reduction by the limit method.

We will now take up the subject of this chapter in detail.

A. STANDARD OF MATTER.

It seems that chemists have not yet felt the necessity of adopting a standard of matter for atomic weight determinations. Therefore the exact and certain determination of the atomic weights of the elements remains yet to be made. The units of these atomic weights, in use for about a century, do not meet the scientific conditions of standards which in physics and even in engineering have been satisfied.

The International Metrical Bureau has not adopted the definitions of a century ago, but the MATERIAL standards which Lavoisier and Hauy were prominent in establishing as members of the commission.

Berzelius adopted oxygen as term of comparison; also in this selection he was far ahead of those who have succeeded him and for a time forced hydrogen upon chemistry as the term of comparison. Since it is well known, that the different determinations of the atomic weight of hydrogen by different chemists of repute vary to the extent of one per cent, it is folly to continue its use. It is characteristic of modern scientific chemistry that the use of such a unit as hydrogen could be seriously considered, and its continued use be made a subject of protracted discussion. Lothar Mayer, Clarke, Van der Plaats and others have adopted or defended the hydrogen unit; Ostwald and some English Chemists, have shown the folly thereof. However, the Meyer-Seubert system is bound to live a long life yet—for it is absurd.

But Oxygen, while infinitely superior to Hydrogen as a term of comparison, is not fit to be adopted as a real standard of matter for an exact system of atomic weights. No gas can be used as such. It would be like using an india-rubber meter standard,

under fixed conditions of temperature and tension. Liquids are also out of the question.

The standard of matter for a system of atomic weights must be solid; compact, to avoid absorptions of gases (Dumas, p. 19); it should be hard, to resist the mechanical effects of handling; it should possess sufficient chemical resistance, to permit the removal of all accidental associations by protracted boiling in aqua regia; and above all, it should be assuredly chemically pure, except such minute mechanical inclusa as will resist the chemical process selected and remain unchanged in weighable form at the close of the process. I know only one element that meets all these requirements. It is the diamond. It is accordingly this substance that must be adopted as standard of matter for our rational system of atomic weights.

Next, it is necessary to adopt a suitable unit. Here it is advisable to conform as much as possible to the units in actual use. Disregarding the hydrogen *unit* for the reasons given, we put the diamond at 12 exactly; for we know, that the oxygen will be nearly 16 and *hydrogen nearly one*, conform to the numbers in use.

Accordingly, the *standard of matter* is carbon in the form of the diamond, and our *unit* is exactly one-twelvth of the atomic weight of this carbon.

Theoretically it would be preferable to adopt half this value as unit; but we can obtain all the theoretical advantages with $C = 12$ and will avoid the confusion that would result from the great change of the unit.

B. THE FUNDAMENTAL DETERMINATIONS OF DUMAS.

Since Moissan has formed a series of crystallized metallic carbides by means of his electric furnace, we may hope that some of these new compounds will be obtained in sufficiently pure form to permit atomic weight determinations. Subjected to the method

devised by Dumas for the combustion of the diamond, the carbide would give, as residue, the oxide of the metal, while carbon dioxide would be collected and weighed.

Until these crystallized carbides shall have been produced in the pure state, we must connect the other elements with the standard of matter by means of the three elements — oxygen, hydrogen and calcium — which have formed the subject of the fundamental determinations of atomic weights by Dumas, and which seem destined to remain the basis of the experimental side of all atomic weight determinations.

The order in which these elements are utilized is as follows: Oxygen, Hydrogen, Calcium.

I. THE ATOMIC WEIGHT OF OXYGEN.

The famous combustion of the diamond was made by Dumas with the object of determining the atomic weight of carbon. But this was an error, due to the Berzelius unit of oxygen being then in use.

The weight of oxygen was not determined by Dumas; the only *direct weighings* he made were those of the diamond and the carbon dioxide produced. A quantity not directly determined cannot be made the basis of systematic calculation; it is affected by all the errors of all the direct determinations of the weighings actually made. It is a dependent variable.

The carbon was weighed by Dumas with precision in the form of diamond — corrected for the residue remaining. The carbon dioxide was also weighed with precision. Our general equations (37) and (38) will, in this case, become, since the common values are $O = 16$, $C = 12$, $CO_2 = 44$, and o designating the departure of oxygen,

$$a = \frac{p}{q} = \frac{44 + 2o}{12} = r + \frac{o}{6}.$$

Hence

$$o = 6\,(a - r) = 6\,e$$

Since no real SERIES of determinations has yet been made, we can take the mean of the actual experiments of Dumas, ranging from 7 to 14 decigrams of diamond; see p. 21. The mean analytical ratio is a = 3.6663, the common atomic ratio is r = 3.6667 rounded off to 4 places. Hence the mean analytical excess is —0.0004 and the *departure* of the atomic weight of oxygen from 16 is o = —0.0024 giving the atomic weight O = 15.9976 or to three places O = 15.998. The atomic perturbation is —0.00015 or 15 units in the fifth place.

It is evident that we need a carefully made series of combustions of the diamond, in which from one to ten grammes of diamond ought to be used in the individual determinations. Such a series will determine whether the true atomic weight of oxygen is 16 exactly.

In most cases we can neglect this minute perturbation of only a ten-thousandth; where that is not permitted, and the results are to be given in their empirical form, we must allow for the departure —0.0024 and the perturbation —0.00015 of oxygen.

There can be no doubt that both departure and perturbation are really zero.

II. THE TRUE ATOMIC WEIGHT OF HYDROGEN.

We have given (p. 21-23) a general exposition of the famous Synthesis of Water by Dumas. His determinations constitute the *first true series* of determinations ever made in this branch of science. In the Comptes Rendus I have presented a preliminary reduction of that series (T. 116, p. 754-756; 1893) such as could be understood directly. Here we can give a complete reduction conform to the principles established in the first part. Table 21 gives all the data in the usual form. Figure 10 represents the same graphically. See pages 178 and 179. It will be

[TABLE 21.]

DUMAS. SYNTHESIS OF WATER.

A. No.	Absolute Weights. Oxygen.	Water.	Analytical Ratio.	Excess. 6th place.	H, Departure. 5th place.
1	13.179	14.827	0.888 852	— 37	38
2	20.362	22.905	976	87	— 88
3	20.495	23.053	9 038	149	—151
19	30.827	34.677	976	87	— 87
16	36.789	41.390	838	— 51	51
8	45.887	51.623	887	— 2	2
10	51.838	58.320	855	— 34	34
11	52.508	59.078	791	— 98	99
4	57.004	64.133	840	— 49	49
	Mean			5.8	— 6
B.					
18	32.133	36.175	0.888 266	—623	631
17	34.162	38.458	294	—595	631
7	34.811	39.178	534	—355	359
6	43.571	49.047	352	—535	544
14	51.838	58.360	245	—644	652
15	56.483	63.577	419	—470	476
9	60.031	67.583	056	—833	641
13	62.090	69.899	282	—607	615
5	76.362	85.960	367	—522	529
	Mean			—576	564
C.					
		ERDMANN AND MARCHAND.			
25	37.034	41.664	0.888 873	— 16	16
26	39.195	44.089	998	109	—110
27	47.321	53.232	957	68	— 69
28	49.460	55.636	993	104	—105
	Mean			66	— 67

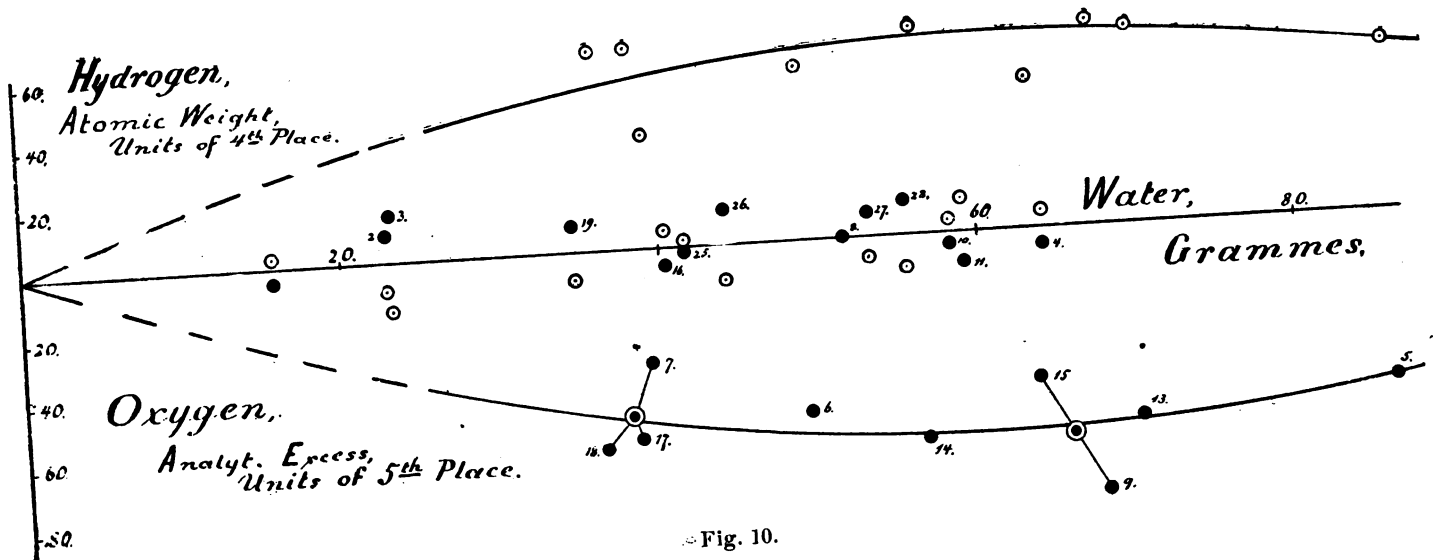

Hydrogen,
Atomic Weight,
Units of 4th Place.
Water,
Grammes.
Oxygen,
Analyt. Excess,
Units of 5th Place.
60.
40.
20.
20.
40.
60.
80.
20.
60.
80.

Fig. 10.

noticed that the analytical excess and the departure are nearly equal but of opposite sign, when they are expressed respectively in units of the fifth and fourth place. Thus the two sets of marks—open circle for departure, filled circle for excess—are almost exactly symmetrically located in reference to the axis of abscissae on which the weight of water produced is set off.

Since in these experiments, the weight of water is determined with the greatest precision, and that of oxygen only by difference of the weighing of the copper oxide tube or bulb, the analytical and the common atomic ratio are

$$a = \frac{\text{Oxygen}}{\text{Water}} \qquad r = \frac{16}{18} = 0.888\,889.$$

In this case, it is more accurate to determine the atomic weight of the hydrogen by calculating the atomic weight x of the water from the experiment, for O = 16, namely

$$x = 16\,\frac{\text{Water}}{\text{Oxygen}} = \frac{16}{a}$$

subtracting 16, and dividing by 2; the departure from unity is given in table 21.

Inspection of the figure or the table shows plainly that the series of Dumas was a *double* one, made under two quite different conditions. The two series cannot possiblly be combined to one though that has been done by Dumas himself and by all recalculators (Clarke, Sebelien, etc.) The nine determinations of Series A all fall close to the axis of abscissae, and give the mean value

$$H = 1.000\,06.$$

The nine determinations B form a parabolic curve, and can therefore not be combined to a mean. The three determinations 7, 17, 18, give a mean that is a mere trifle above the curve, while the mean of 9 and 15 is as much below the curve. This puts all determinations on the curve, excepting No. 6, which remains very little above the same.—The great deviation of No. 5 in the

preliminary curve is here avoided. No. 12 has been omitted by all calculators, on account of a palpable error.

The maximal depression of the curve is 63 in the 5th place for 60 grammes of water, so that u=120, h=0.000 63 (See p. 149). Consequently the coefficients of the parabolic trajectory are, by (25)

$$k = 0.000\,021$$
$$k' = 0.000\,000\,18.$$

These values are approximately two hundredthousandths and 2 ten-millionths only.

Since the curve gives the analytical excess zero for vanishing weight of water formed, the limit of the atomic weight of hydrogen is unity exactly.

Accordingly, the two series of determinations A and B lead to exactly the same result, A direct, B by limit. They are in no way conflicting. But what experimental peculiarities caused this grouping of the determinations of Dumas?

I have repeatedly examined the original paper by *Dumas* (Annales de Chimie et de Physique, T. 8, p. 189-207; 1843) without finding any remark plainly bearing on this fact, which as stated, has remained unknown to Dumas himself, as well as to his revisors and recalculators.

The only statement which may contain the explanation of this divergence is found on page 198, where Dumas says that he is perfectly satisfied if he has established the atomic weight of hydrogen to a twohundredth, that is to half of one per cent, and continues:

"I had intended to reach the thousandth but I have not been able to accomplish it and must leave to more skillful hands the merit to reach that degree of accuracy. It has happened to me that in the same measure in which I increased the amount of water formed and *the duration of the experiment*, diverse causes of error appeared to complicate the weighings and to diminish their precision."

Now, in the experiments A the amount of water produced runs from 15 to 65 grammes, in B from 35 to 85 grammes. For only three experiments of the nine of each series the weights in A were below and in B above the range which they have in common from 35 to 65 grammes. Accordingly, the division into groups A and B is not due to increase in weight.

Nor is this division due to order of succession, or acquired habit of the experimenter, as shown by the enumeration of the experiments in two lines, corresponding to the two groups A and B:

A: 1, 2, 3, 4 ——— 8 - 10, 11 ——— 16 ——— 19.
B: ——— 5, 6, 7 - 9 ——— 13, 14, 15 — 17, 18 —.

Accordingly we are forced to see in this remarkable division of the determinations of Dumas an effect of the *time of the duration of the experiment.* The determinations of series A must have been completed in considerably less time, than those of series B, weight for weight.

We may regret the absence of positive information on this subject in the record of Dumas; but when we consider, that chemists even to-day have not yet grasped the fact that the *amount* in weight operated upon influences the composition of the resulting product, though for thirty years the records of *Stas* have offered the experimental evidence of this fact, we ought to be ready to admire the wonderful chemical acuteness of Dumas, which enabled him distinctly to recognize, fully fifty years ago, both *amount* of matter and *duration* of the reaction as causes of what we now know to be chemical perturbations.

In the table as well as in the diagram, we have entered under Nos. 25 to 28 the four determinations (Nos. 5–8) of Erdmann and Marchand in which they weighed the copper oxide tube after complete exhaustion by an air pump. It will be noticed that their determinations (Series C) coincide with series A of Dumas. Since they used a reduction *tube*, the time occupied in reduction

must have been less than in the experiments of Dumas who used the spherical bulb. We therefore would expect their results to fall into line with series A of Dumas.

As general result we have for all determinations made, H=1 exactly, if O=16, exactly.

III. THE TRUE ATOMIC WEIGHT OF CALCIUM.

After his clear discussion of Berzelius opinion on the hypothesis of Prout (p. 202, l. c.) *Dumas* prefaces his elegant work on the dissociation of Iceland Spar, by saying:

"To verify their (the atomic weight's) accuracy and in order to control the other atomic weights, it will be necessary to enter the way opened by the new analysis of carbonic acid (i. e. his combustion of the diamond); that is to say, we *must make analyses or syntheses on a large scale, effecting very simple reactions on very pure substances.*"

If instead of "large scale" we say a *series* of increasing amounts of matter, this word of Dumas may be taken to-day as the safest guide to obtain the true atomic weights.

Thirty grammes of the Iceland Spar used by Dumas was found to contain 4 mgrs. of silica and 5 mgrs. of ferric oxide; also traces of magnesia and manganese oxide. The total fixed foreign residue is therefore 9 mgrs. in 30 grammes or 0.00030 per unit of weight.

The common atomic weight of Calcium being 40, we have the atomic ratio of the dissociation

$$r = \frac{56}{100} = 0.560\ 00.$$

The results of Dumas' determinations are given in the following table:

DISSOCIATION OF ICELAND SPAR.

No.	Weight in Grammes. Spar.	Residue.	Analytical Ratio.	Excess.
1	49.916	28.016	0.56 123	123
2	50.497	28.305	053	53
3	64.508	36.167	066	66
	Excess due to impurity			30

This would leave an analytical excess of 93, 23 and 36 in the fifth place.

Erdmann and Marchand have also made two determinations on iceland spar, reported in the same volume of the *Annales* p. 213. The analytical ratio was 0.5609 and 0.5618 respectively for about 4.1 and 4.5 grammes of spar. But since this spar contained 0.0004 fixed impurities, the analytical excess would be 5 and 14 in the fourth place.

These authors now prepared artificially pure calcium carbonate with extreme care, and subjecting this product to most careful dissociation, they obtained the following results (l. c., p. 214):

DISSOCIATION OF CALCIUM CARBONATE.

No.	Weight in Grammes. Carbonate.	Residue.	Analytical Ratio.	Excess.
1	8.2335	4.6135	0.56033	33
2	10.8850	6.0940	5985	—15
3	10.1315	5.6740	6004	4
4	5.5310	3.0970	5994	— 6
	Mean			4

A simple calculation will show that this excess produces a departure of 0.004 on the atomic weight of calcium, or a perturbation of 0.0001.

Accordingly, the atomic weight of calcium is 40 with a possible departure of 0.004 and a perturbation of 0.0001.

These dissociations should now be repeated, and regular series of determinations made so that the limit method can be

applied. There can be no doubt but the result will be Ca=40 *exactly*.

IV. RECENT DETERMINATIONS OF THE ATOMIC WEIGHT OF HYDROGEN.

Here we might close this section, were it not for the fact that modern chemists have so long disregarded the value of Dumas syntheses of water, and have so exaggerated ideas about the transcendent importance of more recent determinations of the atomic weight of hydrogen, that it seems advisable to give a summary of these experiments and their bearing on the true atomic weight of hydrogen.

I think this can be accomplished in the best manner by inserting a translation of my Note kindly presented by M. Berthelot at the meeting of the French Academy of Sciences of November 13, 1893 and published on pp. 663-666 of Vol. 117 of the Comptes Rendus. The pages of the original are given in brackets [ ].

[663] "DETERMINATION OF THE TRUE ATOMIC WEIGHT OF HYDROGEN.—BY MR. G. HINRICHS.

"The limit method has permitted us to demonstrate that the absolute value of the ratio H : O is rigorously 1 : 16, taking as basis for our calculations the admirable series of determinations of Dumas on the synthesis of water (Comptes Rendus, T. CXVI, p. 753; 1893). Very careful determinations made by eminent chemists during recent years seem to be in conflict with this result.

"The following are the mean values obtained for the atomic weight of hydrogen, that of oxygen being taken as 16.

E. H. Keiser	1888	1.0032
Cooke and Richards	1888	1.0025
The same	1888	1.0085
Dittmar and Henderson	1890	1.0085
E. H. Keiser	1891	1.000
E. W. Morley	1891-93	1.0075

Considering these values as means, obtained by chemists of equal eminence but by different methods, we must [664] admit that there still remain residual errors, equal to the entire departure affecting H=1. (Comptes Rendus, T. CXVI, p. 696; 1893).

"But we have shown that in Chemistry of Precision it is not admissible to rely on mean values, but that it is necessary to take into account all individual values obtained. Furthermore, we have seen that the residual errors* vary as function of the total weight employed. I have therefore marked graphically, and on a sufficiently large scale, each individual determination by a point for which the abscissa is the weight of the hydrogen employed, while the ordinate is the atomic weight of the hydro-

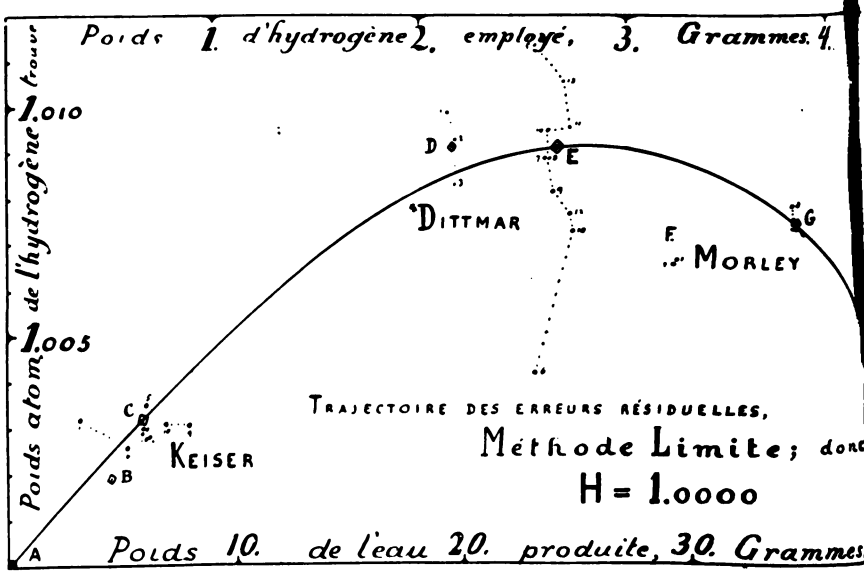


Fig. 11.

gen found. The figure here inserted is a reduction to one-fifth of this graphical construction.

"We see at once that modern chemists have not effected a

*Analytical Excess

series of experiments with variable weights, as Dumas had done; every one of them has confined himself to different determinations for nearly the same weight of hydrogen.

"I am indebted to the kindness of Mr. Edward Morley for the communication, by letter of March 16, 1893, of all unpublished numerical values of his admirably concordant determinations, and he has also permitted me to publish them in graphic form, which can be seen at the regions marked F and G in the above figure. It will be noticed that in the experiments 1 and 2 he has used nearly the same amount of hydrogen, say 3.28 grammes (See F); in the ten other [665] experiments (Nos. 3 to 12) he has also employed almost identical weights of hydrogen, say 3.83 grammes (See G in the Figure).

"Mr. Ostwald has given the mean of the experiments of Dittmar and Henderson in 1891 (Zeitschrift, VII, p. 521); but the mean alone is good for nothing. The *Chemical News* has during last winter, published the numerical values *in extenso*, and I am indebted to the kindness of Mr. F. Dittmar for a copy of the complete Memoir of his father, deceased. I have thereby been enabled to represent the 13 determinations in my drawing; for three of these (D), the weight of the water formed was 19.4 grammes; for the other ten determinations (see E), the weight of the water was very nearly 24 grammes. Dittmar has especially endeavored to perfect the purely chemical part of the problem of the determination of atomic weights; he has most carefully studied all the possible errors of the apparatus used by Dumas, and has succeeded, by remarkably ingenious accessory devises, to avoid them. But the variation from 1.0042 to 1.0114 of the atomic weight found by him shows plainly, that every complication of the apparatus used or of the processes employed only increases the residual errors.

"The ten determinations of Mr. Keiser (American Chemical Journal, X, 260; 1888) have been represented around their mean at C.

"The position of the points C, E and G shows, that the departures from H=1 are undoubtedly some function of the weight of the hydrogen employed. The methods of these three chemists not having been identical, it is not possible to combine them into one series for the rigorous application of the limit method. However, it may be admitted that the three means represented at C, E and G are comparable in degree of precision, each one being the result of about ten determinations on the identical quantities of hydrogen weighing respectively 0.66, 2.66 and 3.80 grammes. The three points mark a parabolic trajectory passing through the origin A.

'The very simple formula

$$d = \frac{h}{5000}\left[5^2 - h^2\right]$$

in which h is the weight of hydrogen used and d the departure of the atomic weight of hydrogen from H = 1, represents sufficiently well the trajectory of residual errors, as is shown by the following table:

	Keiser.	Dittmar.	Morley.
Water produced	5.89	24.0	34.2
Hydrogen employed	0.66	2.66	3.80
d calculated	3.27	9.53	8.03
d observed	3.17	9.12	7.50

[666] "For the limit h = o we obtain d = o; consequently H is rigorously equal to unity. There is, accordingly, no conflict whatever, between the determinations of Keiser, Dittmar and Morley, which to us appear simply as identical values, affected by residual errors determined by the given formula and depending on the total weight put into use. Furthermore, these recent results confirm the masterful determinations of Dumas.

"By letter of April 29, 1893, Mr. Keiser has favored me with some important details about his remarkable method of effecting the synthesis of water at ordinary temperatures. In a preliminary experiment, the palladium absorbed 0.1797 grammes of

hydrogen which combining with 1.4374 gr. of oxygen, produced 1.6169 gr. of water, an amount almost identical with the sum 1.6171 grammes of the gases taken. This experiment gives H = 1.00025. It marks the point A of the figure above given. We await with the most lively impatience the final determinations which Mr. Keiser is going to make soon according to this method, and which probably will give us negative departures.

"It has long been known to be impossible to project a body so as to describe a horizontal line; the greater the velocity of projection the smaller is the deviation from the horizontal for a given distance. In the same way, we have seen here that it is impossible to make the parabolic trajectory of residual errors coincide with that horizontal straight line of which the ordinate is the value of the constant which is sought to be determined by experiments in Chemistry or in Physics."

Since this paper was published, the interesting experiments of Julius Thomsen have given H = 0.9992 (see p. 60). This is 0.0122 below the highest value found by Dittmar, making the total deviation in the different determinations of the atomic weight of hydrogen $1\frac{1}{5}$ per cent!

It is not necessary here to study the new method of Thomsen. The "corrections" or rather "reductions" applied by him are enormous, and the compound reminds us a little of the Consommé Pelouze. At any rate, Thomsen comes within one thousandth of the true value — and is nearer the truth than the more pretentious workers.

C. THE RATIONAL SYSTEM OF ATOMIC WEIGHTS.

We have carefully selected the best possible standard of matter, the diamond. We also have by the process of Dumas, determined the fundamental atomic weights of Hydrogen, Oxygen and Calcium in reference to the standard adopted, namely

C = 12, assumed;
H = 1, O = 16, Ca = 40 exactly, found.

Of the three determined weights, only that of hydrogen h thus far, been obtained by the limit method. Until the sa shall have been applied to the determination of the other t also, it is possible for the empiric to say that the departure these atomic weights may reach a couple of units in the th place.

Now, all other atomic weights are to be determined, by s ple processes of analysis or synthesis, exclusively gravimetric their nature, and best by an application of the limit method.

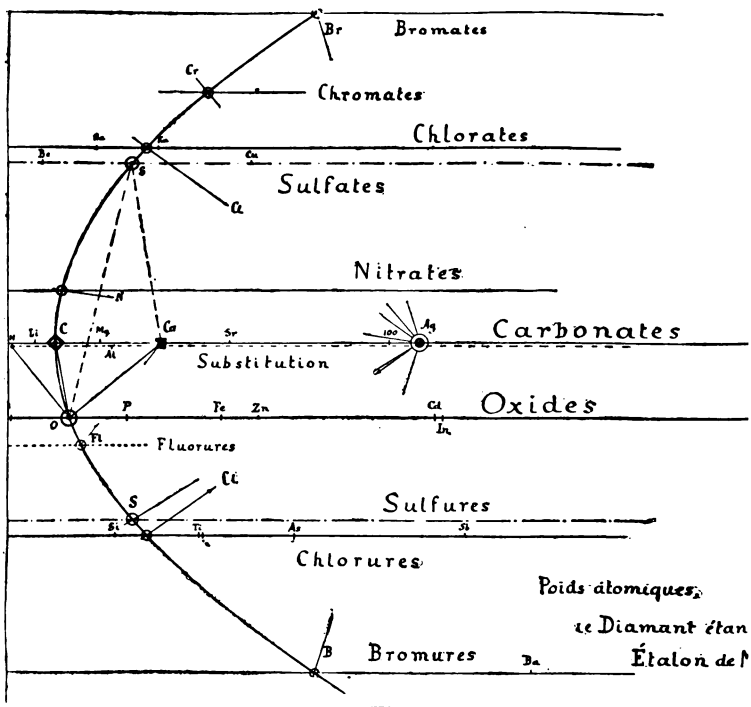


Fig. 12.

Furthermore, we need a graphical representation of the en work, permitting to see at a glance in what manner any gi

atomic weight has been determined, what its departures are, and also showing to the eye the values found.

For that purpose I place the primary element on a parabola and use the secondary axis as the place for the secondary atomic weights determined in reference to the former. See Comptes Rendus, T. 117, p. 1075; 1893. All secondary axes of this curve being parallel straight lines, the atomic weights of all elements will be shown in their true magnitude, if we measure from a line parallel to the common directrix of all.

The dimensions of the parabola are determined by placing carbon in the vertex and calcium in the focus. The vertical zero line therefore is distant 16 from the directrix. Then oxygen, or any other primary element is located on the parabola so that its distance from the zero line measures its atomic weight. On the secondary axis drawn through this point so determined, will be marked all atomic weights determined by means of oxygen, at a distance representing the atomic weight actually found. See Figure 12, which was printed in the Comptes Rendus, and therefore shows the old French terminations *-ures*, instead of our common English *-ides* for binaries. Only the most important details have been entered in this figure.

We have furthermore reserved the *upper* branch of the parabola for ternaries and the *lower* for binaries. Let us consider a few special details.

The OXIDES are located on the secondary axis drawn through the point O, which is that point of the lower branch distant 16 units from the zero line. On this line have been marked the places of H, P, Fe, Zn, Cd, In and Hg, the values of which have been determined by combustion or reduction.

H = 1 exactly, as shown above, by limit method.

P = 31. Schrötter's experiment gives a mean departure of 0.029. Van der Plaats' combustions of yellow phosphorus give —0.023 (Ostwald's allg. Chem., I, p. 101). The mean of these

departures is only 0.003. The mean perturbation accordingly is 0.0001.

Fe = 56. Berzelius reduced the departure to 0.05. Erdmann and Marchand reducing by hydrogen the oxide obtained from ferro-oxalate, obtained (Sebelien, p. 186) in series A the departure —0.0176, while series B gave 0.1072; the general mean is 0.0448. Maumené obtained as mean of six determinations the departure of 0.0016 only.

Zn = 65.5. Berzelius' determinations give the departure 0.10. Morse and Burton's determinations give the mean departure —0.23. These determinations are insufficient, and call for careful repetition, using the limit method.

Temporarily we have to accept the determinations of Gladstone and Hibbert, 1889, though they are not chemical determinations proper, being Faraday's electrolytic equivalents.

For Ag = 108 their mean gives Zn = 65.48 and for Cu = 63.5, their determinations give Zn = 65.54.

The departure is accordingly —0.02 when compared to silver, 0.04 when compared to copper; hence 0.01 as final mean.

Cd = 112. Edgar F. Smith's determinations give the departure 0.055 which represents a perturbation of 0.0005 only. This is very excellent work, such as we have become accustomed to expect from Professor Smith.

In = 113.5, Bunsen, is uncertain.

Sn = 118. Van der Plaats found by 3 oxidations 118.09, by 4 reductions 118.06; mean 118.075, giving the perturbation 0.0006.

Hg = 200. Erdmann and Marchand made careful reductions of the oxide, giving the individual departure —0.0105, 0.111, 0.177, 0.125, the mean of which is 0.101. This represents a perturbation of only 0.0005. As a characteristic curiosity we may mention the manner in which Ostwald (p. 103) spoils the good analyses of Svanberg by using the erroneous value of Stas for sulphur.

Pb = 207. Berzelius, reduction by hydrogen, departure 0.088, and perturbation 0.0004 only.

The CARBONATES are properly represented on the principal axis.

Mg = 24. Departure only 0.0035, according to Marchand and Scherer's determinations, giving the perturbation of 0.00015 only.

Pb = 207. Berzelius' determinations give the departure —0.03, hence the perturbation —0.00014 only.

Li = 7 and Sr = 88 are not sufficiently well determined to warrant the recording of the departure.

The SUBSTITUTIONS BY HYDROGEN are represented on the dotted secondary axis close under the primary axis. We have:

Al = 27. Mallet, measuring the gas, using less than one gramme of metal, mean departure 0.003. Weighing the water, using from 2 to 5 grammes of metal, mean departure —0.003. Mean departure 0.000, and mean perturbation 0.0000.

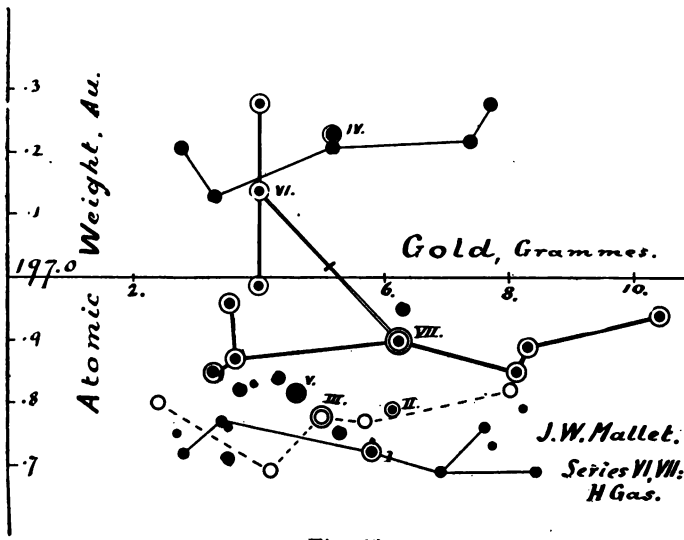


Fig. 13.

Au = 197. Mallet series VI, using 4 grammes of gold, departure 0.14; series VII, using from 3 to 10 grammes of gold,

departure —0.10. Mean departure 0.04 corresponding to a perturbation of 0.0002. The diagram Figure 13, here given, represents all the results obtained by Mallet according to his own calculations, American Chem. Journal, XII, kindly sent me by the distinguished author. We regret that we have not room to dwell upon the many interesting and instructive points which this diagram presents to the eye.

The atomic weight of SULPHUR is determined both by using the sulphate and by the sulphides. Erdmann and Marchand converted the residual lime from purest Iceland Spar into Sulphate, and found (Annales de Chemie, T. 8, p. 216; 1843).

	Weight, grammes.		Analytical.	
No.	Spar.	Sulphate.	Ratio.	Excess.
1	2.370	3.225	1.3607	7
2	4.796	6.5255	6	6
3	3.065	4.1690	2	2
4	5.446	7.4100	6	6
Mean.....	4.0	.....	5	5

Since $CaO_3C=100$ and $CaO_4S=136$, these determinations give for the departure of sulphur 0.05. The limit method applied to the sulphids gives $S=32$ exactly; we shall, therefore, use this value exclusively.

On the secondary axis passing through this point, are marked the atomic weights of Be and Cu determined from their sulphates

Be=9. Departures 0.027, Krüss, 1891.

Cu=63.5 exactly, according to my critical recalculation of Richards determinations, see p. 128-136 supra.

The three determinations (1, 2, 3) of Erdmann and Marchand (Sebelien p. 178) made in 1844 on about 63 grammes of Copper Oxide gave a mean departure of —0.014 and consequently the perturbation of —0.000 22 only. This result of 1844 is nearer the truth than that of Richards half a century later, as published by himself; his departure is 0.11 and perturbation 0.00172.

Sb = 120. The researches of Schneider in 1856 and 1880 on the reduction of native sulphide, and those of J. P. Cooke on the synthesis of sulphide, prove that the departure is zero, at least in the second place. The perturbation can, therefore, not exceed a few units in the fifth place.

The secondary axis for FLUORINE is very well determined by the analysis of *Louyet* (Annales de Chimie, T. 25, p. 300; 1849; see also, p. 27 supra) in which he secured the complete conversion of pure fluorspar into its sulphate. The atomic ratio is 1.743 590; the mean analytical ratio is 1.7436 which is identical to the fourth place. We have therefore Fl=19 exactly, practically.—Moissan has recently made corresponding determinations, of which those on his artificial *crystallized* calcium fluorids are the most important. I regret very much that I have not been able to obtain the necessary weighings of these determinations; for neither the Comptes Rendus, nor the Annales de Chimie, give these data.

In order to obtain the exact position of the secondary axes for the CHLOROID ELEMENTS, and for NITROGEN and SULPHUR, we can utilize the determinations of Stas. We have seen that for Ag=108 exactly, these atomic weights are 35.5, 80, 127, 32 and 14 exactly, according to our limit method. It remains therefore, only to determine whether the atomic weight of silver is 108 exactly, or not. This determination I have given in a *Note* presented at the meeting of April 25, 1894; see Comptes Rendus, T. 118, p. 944.—The following is an exact translation of this Note.

"COMPARISON OF THE SECONDARY STANDARD WITH THE DIAMOND STANDARD."

"We have to go back half a century before we can find sufficiently accurate experimental researches allowing us to connect the atomic weight of silver with that of the diamond. Silver carbonate not being suitable, it was necessary to use the acetate,

conform to the example of Liebig (1841). The method of investigation had most closely to resemble that of Dumas of the same year. This research has been carried out in an admirable manner by E. Maumené; see Annales de Chimie et de Physique, T. XVIII, pp. 57-61; 1846.

"He took "very beautiful crystals" of silver acetate, and heated them in a current of air completely freed from carbonic acid. He weighed the residue of silver, p and also the carbonic acid produced q. Since the acetate contains two atoms of carbon for each atom of silver, we have CO_2 being 44 exactly,

$$Ag = 88 \frac{p}{q}.$$

"Maumené made 5 determinations of which the results are here given.

No.	p	q	Ag
1	8.083	6.585	108.0188
2	11.213	9.135	108.0372
3	14.351	11.6935	107.9992
4	9.030	7.358	107.9968
5	20.227	16.475	108.0410

"the mean of these very concordant experiments is 108.0186; but it is not the mean, but the *true* value, which we desire to find.

"Analyses Nos. 3 and 4 were made with substance obtained by recrystallizing beautiful crystals, prepared in large quantity, and used for the analyses Nos. 1 and 2; for analysis No. 5, the salt was prepared on a small scale from silver chloride. If we designate the purest substance by A, and the least pure by C the five determinations arrange themselves in the following order:

	No.	Weight, p grammes.	Ag	Deviation from mean.
A	3, 4	12	107.9980	0.0012
B	1, 2	10	108.0280	0.0092
C	5	20	108.0410	.....

"As we might have expected, the concordance of the individual results is greatest for the purest material. The result A

is therefore nearest to the true value. The departure from 108 is 0.041 for C, 0.028 for B and only –0.002 for the purest material designated by A. The corresponding perturbation is only —0.00002. We may, therefore, accept 108 as the true atomic weight of silver, the true expression of the experiments of Maumené.

"Marignac has made three determinations by simple dissociation of silver acetate; the most carefully purified salt was used in the third of his experiments. From the data published by Sebelien (p. 76) I find for the first two determinations 107.969 and 107.945, the mean of which is 107.957; and for the purest substance used in the third determination, I find in the same way 107.976. The departure has been reduced from 43 to 24 thousandths by the recrystallization; the true atomic weight is 108. But the method of Marignac is subject to several errors which are guarded against in the operations of Maumené; the value of Marignac is therefore, simply confirmatory.

"For the final solution of this problem, it will be necessary to return to the method of the masters. The compound recommended by Liebig will have to be submitted to the processes of Dumas, and an entire series of such determinations will have to be made in order to obtain data which will allow the rigorous application of the limit method. I may be permitted to acknowledge, I am convinced from the results already obtained, that the true atomic weight of silver is 108 exactly, that of the standard of matter, the diamond, being 12.

"In these later years, the applications of electricity have required very careful electrolytic determinations for the comparison of ampèremeters. We may utilize these researches for the determination of the atomic weight of silver, that of copper having been determined with precision, 63.5 exactly; see my recent Note, Zeitschr. anorg. Chemie, V, p. 293—298; 1893 (supra pp. 129—136).

Let k represent the eletrolytic equivalent of silver, then its atomic weight will be

$$Ag = k. \frac{Cu}{2} = 31.75\ k.$$

"The first careful determinations of k we owe to Lord Rayleigh; they are published in the Philosophical Transactions for 1884. This Serial not being accessible to me, I see in a Note by W. N. Shaw (Phil. Mag. XXIII, pp. 136—141; 1887) that Rayleigh found 3.405 and 3.408 with a current density of 0.012 ampères and 3.404 with 0.026 ampères per square centimeter. From the investigations of Gray (Phil. Mag. XXII, p. 389—414: 1886) and from those of Shaw on secondary influences, it seems to me beyond doubt that the determinations of Rayleigh represent an upper limit. Accordingly we have

		K	Ag
1884	Lord Rayleigh	3.404	108.047
1886	Thomas Gray	3.4013	107.997
1887	W. N. Shaw	3.3998	107.944

"The mean of the extremes is 107.995; and the corresponding determinations seem to possess the same degree of precision. The value of the extremely careful determinations of Gray differs from that mean by 0.002 only. This represents assuredly a most remarkable confirmation of our value 108.

"For my values of atomic weights (H = 1. O = 16, S = 32 exactly) the well known formula of blue vitriol requires 25.451 per cent. of copper, if the atomic weight of copper is 63.5 exactly. The three series of electrolyses of T. W. Richards have given him the values 25.455, 25.450 and 25.448. The mean of these extremely concordant results is 25.451, which is exactly identical with my calculated value."

It may be proper to add, that the discarding of the determinations 1, 2, 5 of Maumené is in strict accord with the fundamental, I might say the self-evident principle, that only the

purest materials can give the most reliable results. Compare p. 147 supra. Such a proceeding is *not* an arbitrary selection — but a classification of results according to the qualitative limit method.

D. NEW EXPERIMENTAL RESEARCHES REQUIRED.

My critical review of the existing atomic weight determinations has been carried on far beyond the results recorded above. I regret to say that the general outcome of this work is very unsatisfactory. Most experimental determinations have been made as if planned by that novel character of Holberg's Comedy "den Vägelsindede," whose leading peculiarity was the manifestation of a new mood every minute. In the same manner, our modern chemists make one or a couple of determinations of an atomic weight under certain specified conditions, and presto, change the conditions anew, to introduce new unknown quantities, new residual errors! In the light of the principles here established, such procedure is essentially a waste of time and labor. I have therefore not encumbered these pages with the results obtained which are simply approximative.

By the establishment of the limit method, a corresponding new period in the experimental work becomes necessary. It is greatly to be hoped that those in charge of prominent laboratories will appreciate these requirements. The reward will be most gratifying.

The new requirements have been sufficiently set forth in this Second Part. Every determination requires the execution of a true series of analyses, identical throughout in every way except in the amount of matter operated upon. Thereby the function of perturbation is determined empirically. Only the amount of matter, the independent variable, is gradually to change, best in an irregular manner, so as to obtain determinations of the dependent variable for the entire interval for which such a series can be made with precision.

No such enormous quantites as have been used by Stas should ever be employed again. Some of his determinations on 400 grammes of silver we have found to be affected with an error of reduction to vacuum amounting to 68 milligrammes; the pretended limit of accuracy was therefore illusory.

But if the limit of weight be placed at 40 grammes, and determinations made to the milligramme, the accuracy would be 7 times that of Stas in his worst case. For this amount the actual uncertainty will now probably not appreciably exceed one fifth of a milligramme, which raises the precision to thirty-five times that noted case. For the lower limit, in the neighborhood of four grammes, a fiftieth of a milligramme may now be approached to in the best cases. In other words, the analytical ratio may be recorded to the unit in the fifth place.

It is also quite evident that this synthesis is not necessarily preferable say to a carefully made electrolysis. Instead of accepting the challenge of Stas it will be much more beneficial to subject carefully prepared silver nitrate to a properly conducted electrolysis.

Dissociations are also more generally to be used, provided they can be thoroughly controlled. The process of Dumas, as applied by Maumené to silver acetate, will prove very useful in a larger field. The dissociation of purest Iceland Spar should be effected in a platinum apparatus, so as to permit the separate collection of accessory volatile constituents in a distinct set of absorption tubes below a definite temperature, while the dissociation products proper are collected at a determined interval of temperature above that lower limit. Traces of bases other than lime to be determined separately.

But it would be manifestly improper to attempt more than such suggestions while pressing the invitation to this new field of atomic weight determinations according to the conditions of our limit method. Only those chemists who may be inspired to this

great work will undertake it, and they will soon ascertain the proper experimental conditions for themselves, much better than we can conceive of.

The real work of the experimental determinations of the true atomic weight of the majority of the elements remains yet to be done. If it is begun soon, it may be reasonably well completed during the next quarter of a century.

The true chemists of to-day will recognize with me the necessity of this division of labor. At any rate, even if I possessed all the means necessary, and also were endowed with the sum of experimental skill of all the best "performing chemists" of the day, it would be folly to undertake this work; for it is clearly the work of a generation and not of an individual.

THE EMPIRIC MODERN CHEMIST IN THE JAHRBUCH DER CHEMIE.

But not all chemists are true scientists. In one country chemists are getting to be so numerous as to constitute a distinct craft (handwerk); and, reciprocally, many good craftsmen (handwerker) in that country fondly imagine they are great chemists. Such chemists can write up a fair synopsis of new facts and simple experimental details for the Jahresberichte or for some Jahrbuch; but when they undertake to * report on a broader and deeper chemical subject they make as interesting a spectacle of themselves as did "Karlen" in Berzelius Laboratory when called upon to define chemistry. It seems never to have dawned upon their minds that the SCIENCE OF CHEMISTRY comprises something beyond the mixing of liquids, the obtaining of precipitates and the producing of vile stinks to make it unpleasant for "Karlen" to clean up the dishes and things. Even the definition of *Lemery*† of two centuries ago proves too ample for their narrow ideal of chemistry, for they make a consommé.

* "Honestly" we should have inserted—but there has been an A. Naumann, and several others of that kind.

† Chemistry 's an Art which teaches to seperate the different substances contained in a Mixture.—

To these chemists it seems preposterous to submit the results of Stas or of any other good analyst to a rigorous discussion; they assert that only new facts, new experiments, new determinations are needed. They do not seem to know that they themselves are producing too many facts not properly established. that they make too many experiments not teaching us anything with certainty, and that they are publishing too many determinations that determine nothing or something entirely different from what they teach. In twenty-five years from now the bulky productions of such chemists will stand on the dusty shelves of the libraries and be looked upon by the chemists of the day with a shudder akin to that we feel when looking upon many of the enormous foliants of the fathers and scholasts. — Berichte!

There are to-day "prominent chemists" in Germany, editors of chemical journals and paid compilers of Jahresberichte and Jahrbücher, who are as utterly innocent of all knowledge of the fundamental principles of SCIENCE in general, as was their "*prototype*" who reported on the discovery of Kepler's first two laws in the "Jahrbuch der Astronomie für 1610" saying in the quaint German of that time:

"Mr. Kepler has made some remarks * de motibus stellæ martis, with critical notes on a fancied elliptical rather than the accepted circular orbit of that fiery planet; *however* (uebrigens) *Mr. Kepler has furnished no new observations of his own* to sustain the strange ideas† which he has advanced."

That reporter was evidently in blissful ignorance of the fact, that the observations used by Kepler constituted the entire life-work of the greatest observer and most talented deviser of methods and instruments, the builder of Uraniborg, Tycho Brahe; he was equally ignorant of the fact that Tycho never pretended to be able to completely reduce his observations;

* Aeusserungen—the modern technical term for statements of fact or mathematical deductions not comprehended by the reporter.

† Laws in precise mathematical form, fully demonstrated by facts — are not understood; so they call them "ideas."

finally, history has practically proved that the brutes in power at the Danish court were providentially permitted to drive the grand old astronomer from Hveen into exile and death in order that the wonderful observations might come into the hands of Kepler, who did unravel their hidden meaning because of his special talents for such work, which necessitated that he himself never was much noted as an observer. Nature practices the devision of labor, "Signor Crisso, mio dolce;" it has not produced an animal combining the qualities say of the ass and the lion; when imitated, the bray betrays the donkey, "Signor Crisso, mio bello."*.

It needs only this simple statement of a reasonably parallel case to characterize the real scientific standing of certain "prominent chemists" in leading Universities of Germany. Their actual experimental work may, as commonly expanded, fill hundreds of pages in the Annals of Chemistry of the Land of Liebig; and that work may happily be drowned in the immense mass of that kind now being printed; but the chemist who perpetrated that parallel statement in the pages of the Jahrbuch der Chemie für 1893 (p. 49) is sure of a leather medal, triple size and double thick, and his name is bound to retain forever the unspeakable freshness of his statement.

No one can feel a deeper interest or even pride, than I, in the well established renown of the numerous truly great scientists which the hardy and thoughtful race occupying the old Fatherland in the very heart of Europe, has produced, to the glory of Germany and for the benefit of the entire human race. But I cannot forbear to express a feeling akin to disgust, when in the very shadow of the lecture stand of the great LIEBIG I see the professor of Chemistry write for the pages of a Jahrbuch der Chemie—a report precisely like the one of 1610 quoted above, which is the exact equivalent to the statement that the law of gravitation is not true, because, forsooth, Newton† himself did not measure the meridian that gave him the required dimension,

*Galilei, Postille al libro del Rocco. Ed. Milano, 1832, T. 2, p. 177-178.

† Principia, Book III, Propos. IV, Theorem IV (Davis, London Ed., Vol. II, 1819, pp. 169—170).

nor personally carry the clocks from one continent to another and observe in their changing rate the varying distance from the center of the earth. — O grandissime bue!

Possibly Professor Krüss of Munich may yet prove one of the most useful of that empiric strain (p. 84. footnote) now in place and power; for he has given a most glaring picture of German chemical SCIENCE which, as it seems impossible to reach a lower depth of empiricism and narrow craft-cunning, must necessarily, when the change comes, rise to a broader and higher scientific level. I hope it may reach up again to the exalted position in which the true masters left it years ago.

Firmly convinced that I have demonstrated, by the use of the experimental determinations of the Old Masters and of Stas, the power and capacity of my limit method, I believe that the experimental work required to apply this method rigorously to all elements will be done in the best manner by the generation of chemists now students in the lecture halls and laboratories of the universities throughout the world.

It is not this multitude that will do the work here planned. The multitude exerts a depressing influence to-day in Science as it did five centuries ago in the Church. But there always will be individuals of high aims, and endowed by a kind nature with gifts not conform to the mean. It is to such individuals that the purely scientific work here mapped out will prove enticing. While the great multitude will in science only see the modern ladder to position and wealth, these "foolish" individuals will be happy if they obtain an opportunity to devote all their energies to the establishment of the fundamental constants of nature, the true and exact values of the atomic weights of the elements.

To these true chemists, to whom we must look for the great work indicated, I say with Dante (III, x, 22-25):

Or ti riman, Lettor, sovra'l tuo banco,
Dietro pensando a ciò, che si preliba,
S'esser vuol lieto assai prima, che stanco.
Messo t'ho inanzi: omai per te ti ciba.

PART THIRD.

THE COMPOSITION OF THE

CHEMICAL ELEMENTS

AND THE

UNITY OF MATTER.

I. INTRODUCTORY.

The subject of this part was originally reserved for the third volume of my Elements of Atom-Mechanics. But while the relations between the composition of the elements and their chemical and physical properties require of necessity at least two additional large volumes, it has seemed advisable to include a mere outline of the general results obtained concerning the atomic structure of the elements in this first volume.

I may as well admit that I am also influenced by a somewhat personal reason to discount a portion of the contents of a subsequent volume of my Atom-Mechanics. When the colors begin to tint the evening sky the diligent husbandman finds much to do calling for renewed energy.

In all works on chemistry published during the last dozen and more years, the so-called *Periodic Law* occupies a prominent place.* Having suddenly been universally accepted in a most empiric age, is proof sufficient that it is not true to Nature. It is, in fact, nothing but an empirical and largely erroneous transcription of an imperfectly comprehended part of my Programme of Atom Mechanics of 1867.

*The only sound criticism of this so-called law I have seen in print is that of Berthelot, in his fascinating work Les Origines de l'Alchimie, Paris, 1885; p. 312, and others.

The facts in the case are simply matters of record, furnished by publications of well known dates. Any one of sufficient knowledge could at any time set this case right, by simply cutting loose from the misleading tutulage of the German Jahresberichte and turning to the original publications for study.

Having presented the true atomic weights, we may now add the true system of the chemical elements, and incidentally show the modus operandi of the discovery of the "periodic law" by one of the coryphees of German Chemistry.

I firmly believe, that the time will come when in the universities of the world the exposition of the true constitution of the elements will replace that false and fraudulent empirical transscription of the same now almost everywhere taught under the name of the periodic law.

One of the striking peculiarities of this empiric fraud is its co-existence with the belief that the atomic weights of the elements are not exact multiples.

Our great chemists, like Ostwald, do not seem to comprehend that if the "exact multiples" are a chimera, any periodic law of the atomic weights must be an impossibility. How much of his "Schluss" (pp. 137-138, l. c.) would have become clear to Professor Ostwald, if he had discarded the Jahresberichte and examined for himself my work of 1867, of which several copies are at Leipzig!

But enough of preface. We must try to be brief. Let us proceed to consider the atomic weights of the elements and examine whether they are *exact* multiples of half the atomic weight of hydrogen, or not.

II. THE ATOMIC WEIGHTS ARE EXACT MULTIPLES.

In the first place it will be admitted that only those elements can be considered in this question for which the atomic weight

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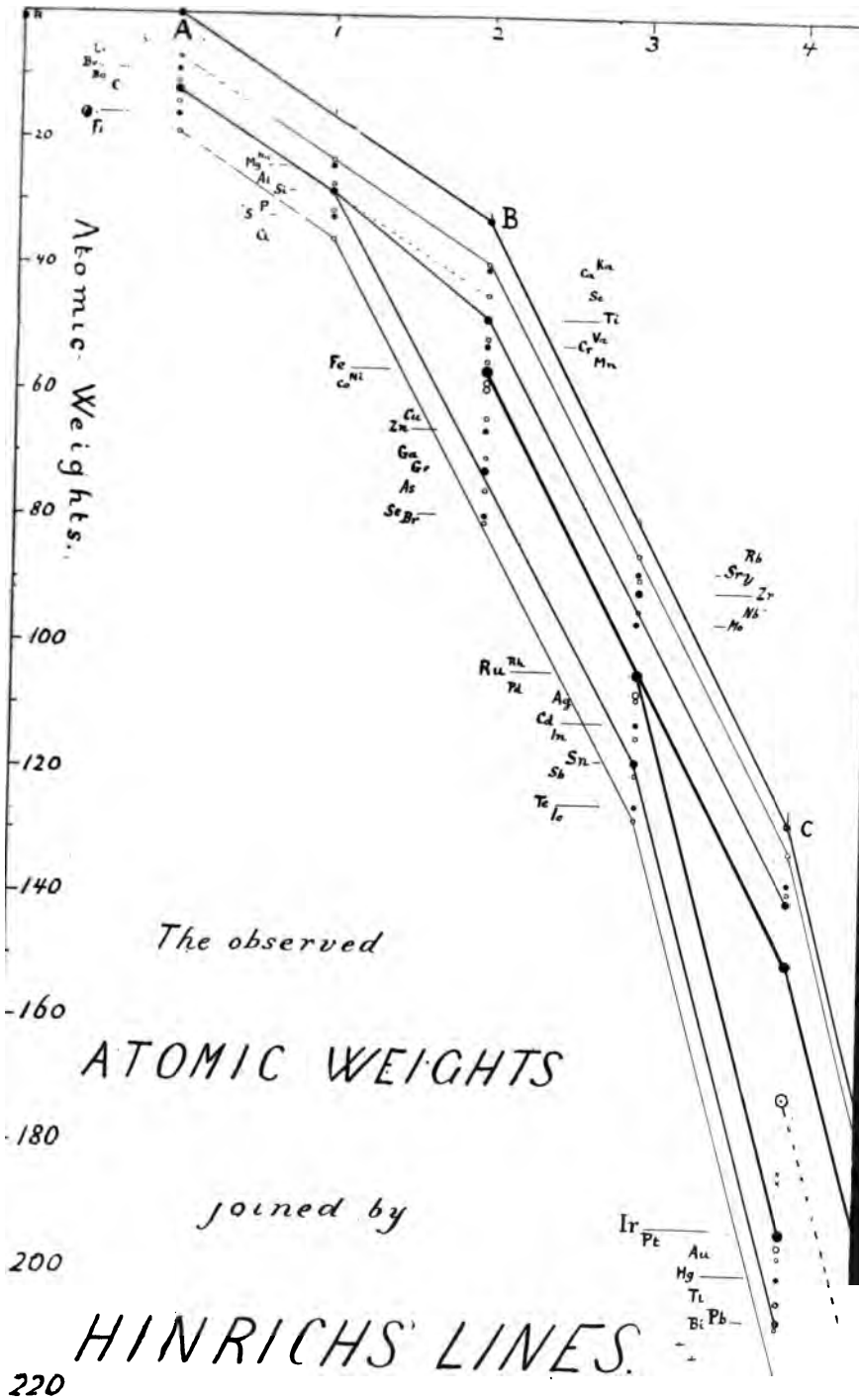


The observed

ATOMIC WEIGHTS

joined by

HINRICHS' LINES.

ith precision and certainty. This will throw out all
hich themselves are imperfectly and incompletely
ecially the following 14: Sc, Y, Zr, Nb, La, Ce, Nd,
Dp, Yb, Ta, Th.

we possibly make any use of the determinations for
ents: Be, Bo, Ti, Va, Ga, Ge, Mo, Wo, Ur; for all
hat the atomic weights of these elements are very far
known with precision and certainty.

following 26 elements the nearest unit is in most
n; but the atomic weight of none is known with pre-
r example, the unit even is somewhat in doubt for
also whether their atomic weights are equal or not,
h of these elements are comparatively common. New
are imperatively called for, rather than premature
nanufacture the same for pelf. The Kaloids Li, Na,
awn into the charmed circle of Stas; but his results
lements we have shown to be worthless. For Anti-
ve a famous research of J. P. Cooke giving 120 ex-
s there are conflicting data, it may be best not to in-
result at this time, to avoid possible opposition. The
rches of Richards on Barium give exactly 137.5
rly reduced; but as he operated on the Consonmé
work is without weight. We have apparently good
few others; but the determinations of
metals are extremely difficult. The
e or less common elements for which
t known with that degree of certainty
r our purpose: Li, Na, Si, Ka, Cr,
In, Sb, Te, Cs, Ba, Tl, Bi; also the
Pd; Os, Ir, Pt.

ain only the following 22 elements for
ess reasonably accurate and certain
ic weights, namely: H, C, N, O, Fl,

Mg, Al, P, S, Cl, Ca, Fe, Cu, Zn, Br, Ag, Cd, Sn, Io, Au, Hg, Pb. This list includes certainly the most important of all elements.

The following table gives the data, collected from Chap. III, C, Part II.

TABLE OF ATOMIC WEIGHTS ESTABLISHED.

C=12, standard of matter. Determined by limit method: H=1, Cl=35.5, Br=80, Io=127, S=32, N=14, all exactly so, except perhaps Io.

Determined numerically, not yet by limit method:

Symbol.	Weight.	Departure 3rd place.	Perturbation 4th place.
O	16	-2.4	-1.5
Fl	19	0	0
Mg	24	3.5	1.5
Al	27	0	0
P	31	3	1
Ca	40	4	1
Fe	56	1.6	0.3
Cu	63.5	0	0
Zn	65.5	10	2
Ag	108	1.2	-0.1
Cd	112	55	5
Sn	118	75	6
Au	197	40	2
Hg	200	101	5
Pb	207	88	5

The perturbations of these elements are summarized in units of the fourth place as follows:

ABSOLUTE ZERO, determined by the limit method.....7 elements.
ZERO in fourth place; Al, Cu, Fl.....3 "
Less than HALF a unit: Ag, Fe.....2 "
ONE unit, less than 2: Pb, O (neg); Ca, P, Mg (pos). 5 "
TWO units: Zn, Au.....2 "
FIVE units: Cd, Hg.....2 "
SIX units: Sn.....1 element.

Now for FIVE units the atomic weight departs 5 in 10,000 or 1 in 2,000 only. Suppose we take that as the UPPER LIMIT, so that we must admit that Cd, Hg are on this limit and Sn just above it. We have accordingly left the following elements, the perturbations of which have been found not to exceed one in five thousand:

Perturbation	0	1	2	3	4
No. of Elements	10	7	2	0	0
Calc. No.	10	6.92	2.29	0.36	0.03

Applying my formulæ for the probability to the data given we obtain the calculated number of elements of the last line, which practically agrees with the observed number. See p. 48 of my work of 1893 quoted p. 41.

Out of a total of 19 elements, 10 show a perturbation zero, 7 show a perturbation of 1 in 10,000 and for 2 elements the perturbation is 1 in 5000. This proves most assuredly that all of these atomic weights are *exact* multiples in fact.

In addition to these 19 rigorously and strictly conform, we have 3 elements (Cd, Hg and Sn) for which the perturbation reaches 1 in 2000 and for which new determinations might be desirable.

Figure 14 gives a graphic representation of these facts. The ordinates represent the *number* of elements for which the *perturbation* (in 4th place) is measured by the abscissa. The scales indicated show that the perturbation zero marks the limit of H=1 exactly by a length of fifty meters. That is, on the scale of this drawing, the unit of atomic weight for which the perturbation is given (5mm for 0.0001) measures 50 meters. To properly appreciate the dimensions represented in this drawing, we must remember that H=1 exactly would end at perturbation zero (middle ordinate of the drawing) and extend 50 meters to the left! The mere inspection of the drawing therefore shows

that for the 19 elements the perturbation outstanding is actually nothing or absolutely insignificant, and even for the other three elements (Cd, Hg, Sn) entirely within bounds; by the application of the limit method, the perturbations will, no doubt, all be found to be absolutely zero.

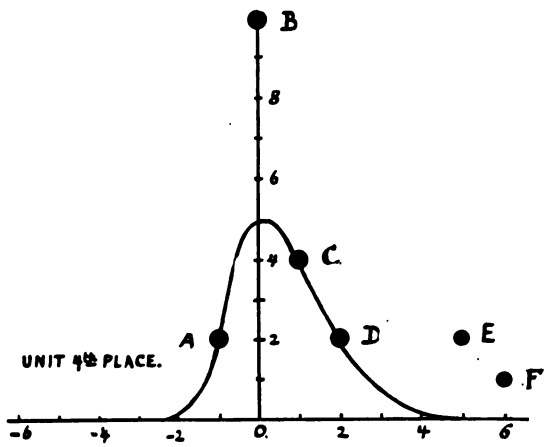


Fig 14.

The points determined represent the experimental data given above as follows: Point A represents the mean of O and Ag. Point B represents the 7 elements submitted to limit method and the three elements for which the perturbation is zero to the fourth place. In point C are represented the 2 elements P and Ca as well as the mean of the two Fe and Mg; hence 4 in all. Point D represents the 2 elements Zn and Au. Point E represents Cd and Hg, and F represents Sn.

The middle ordinate is excessive; so it should be if the perturbation zero is the law, and minute deviations the exception due to experimental shortcomings in the absence of the limit method. By taking C and D, a simple calculation or construction according to my methods of probability already mentioned, gives for perturbation zero the value 5, by means of which the full drawn PROBABILITY CURVE has been traced in the diagram.

It is perfectly clear that the residual perturbations follow the law of probability as closely as can be expected. Though, therefore, the elements not yet subjected to the limit method, give a residual perturbation, the values thereof for the different elements are distributed around the zero point in accordance with the law of probability. Consequently, the ZERO is the TRUE PERTURBATION also for these elements.

This completes, I think, the demonstration that the atomic weights of the elements are exact multiples of that of Hydrogen or in a few cases, of half that value. It removes the objection* commonly urged that by diminishing the value of the multiple, it will go in any set of given numbers inside of residual errors of experiment.

Since the 22 elements considered comprise the most important of all, and are the only ones for which sufficiently precise determinations have been made, it is legitimate to conclude, that as soon as the other elements shall become as well known and have their atomic weight determined with the same degree of precision and certainty, they will give a like result, namely, that the atomic weights of the elements in the great majority of cases are exact multiples of that of hydrogen, while in the few exceptional cases they are exact multiples of half the atomic weight of hydrogen.

What for over a quarter of a century has been descried as a chimera is therefore a scientific fact. The UNITY OF MATTER is the logical and necessary conclusion from this fact.

III. SPECIES AND GENERA OF ELEMENTS.

The chemical elements are properly considered to be individual specific forms of matter, which thus far have been neither changed one into another, nor decomposed in any manner. Each of these SPECIES of matter is designated by the Berzelian

* Best presented in Berthelot, Alchimie, p. 292-293.

(latin) Symbol, and characterized by its atomic weight. Example: N, 14.

To this characteristic we have added the ATOMIC FORM AND DIMENSIONS. See Am. Jrl. of Sc., Nov. 1866, Vol. XLII, also Programme der Atomechanik 1867, p. 7. Really, this dates back to 1855; see p. 54 supra.

Chemists have long ago recognized certain GROUPS of elements most closely resembling one another in their chemical and physical properties. I have more precisely characterized these groups by their relations as to atomic weight and form, and consider them truly GENERA of matter, which I have designated by a simple NAME (in oid) and a GREEK SYMBOL. See Atomech. p. 6-10.

Of the genera given in the work referred to and which are entirely beyond doubt, I will here enumerate the following:

GENERA.		SPECIES.				
Symbol.	Name.	Order: 0	1	2	3	4
χ	Chloroids	Fl	Cl	Br	Io	?
θ	Sulphoids	O	S	Se	Te	?
ϕ	Phosphoids	N	P	As	Sb	Bi
$K\delta$	Cadmoids	Be	Mg	Zn	Cd	Hg
$\chi\alpha$	Calcoids	"	"	Ca	Sr	Ba
$K\alpha$	Kaloids	Li	Na	Ka	Rb	Cs
$K\upsilon$	Cuproids	"	"	Cu	Ag	Au

These genera were grouped 1867 in my Atommechanik in a radical figure, Fig. 15, the radii marking the genera, and the spiral cutting them according to the order number, the distance of the species from the center being proportional to its atomic weight. Plate VII shows a more carefully prepared large wall chart of that time. For ordinary print this form was changed to a system of parallel lines, which were arranged according to the atomicities and electrical character. We shall come back to these subjects.

A very important fact is also the relation of the Cadmoids to the Calcoids, which was represented by a *branching* radial line on the diagram.

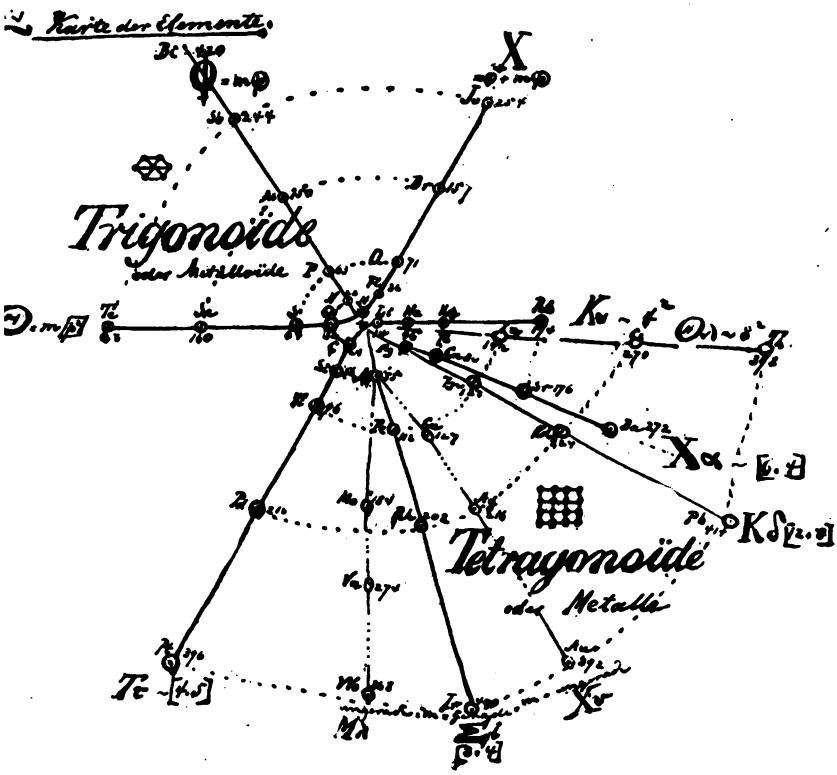


Fig. 15.

To the above genera are yet to be added modifications of $\Sigma\iota$ and $T\tau$, the iron groups and also a number of groups of rare metals. In general, I omitted the rarer metals in 1867 on principle, precisely as we are, on the whole, compelled to do even today, because they are not sufficiently known. We have had an interesting instance thereof in Section II.

It should be added, that while the Berzelian latin symbol of a species represents a *number*, the atomic weight of the ele-

ment, my Greek symbol of a genus represents a *formula*, namely, the algebraic expression of the atomic weights of *all* the species of the genus, as functions of the *order number* of the species.

It is also apparent that these generic symbols permit the representation of generic reactions and entire classes of compounds. For example: KaX, XaX_2, $A\delta\theta_2$.

IV. SYSTEM OF THE ELEMENTS.

The first more comprehensive publication of my System of Chemical Elements was made in my *Programme der Atomechanik*, 1867. Adapted to letter press, by substituting parallel lines for the radii, in my publications of 1869. Final, important modifications and additions were presented in my Principles of Chemistry, 1874 (Sect. XVIII, pp. 178-182). To this nothing need be added even to-day, in principle.

But instead of giving a historic exposition it will conduce to clearness and secure the desired brevity for this part if we present our System as the result of *direct induction*.

The best characterized genera of elements are the Kaloids and the Chloroids, constituting the electro-positive and the electro-negative extremes of the entire system.

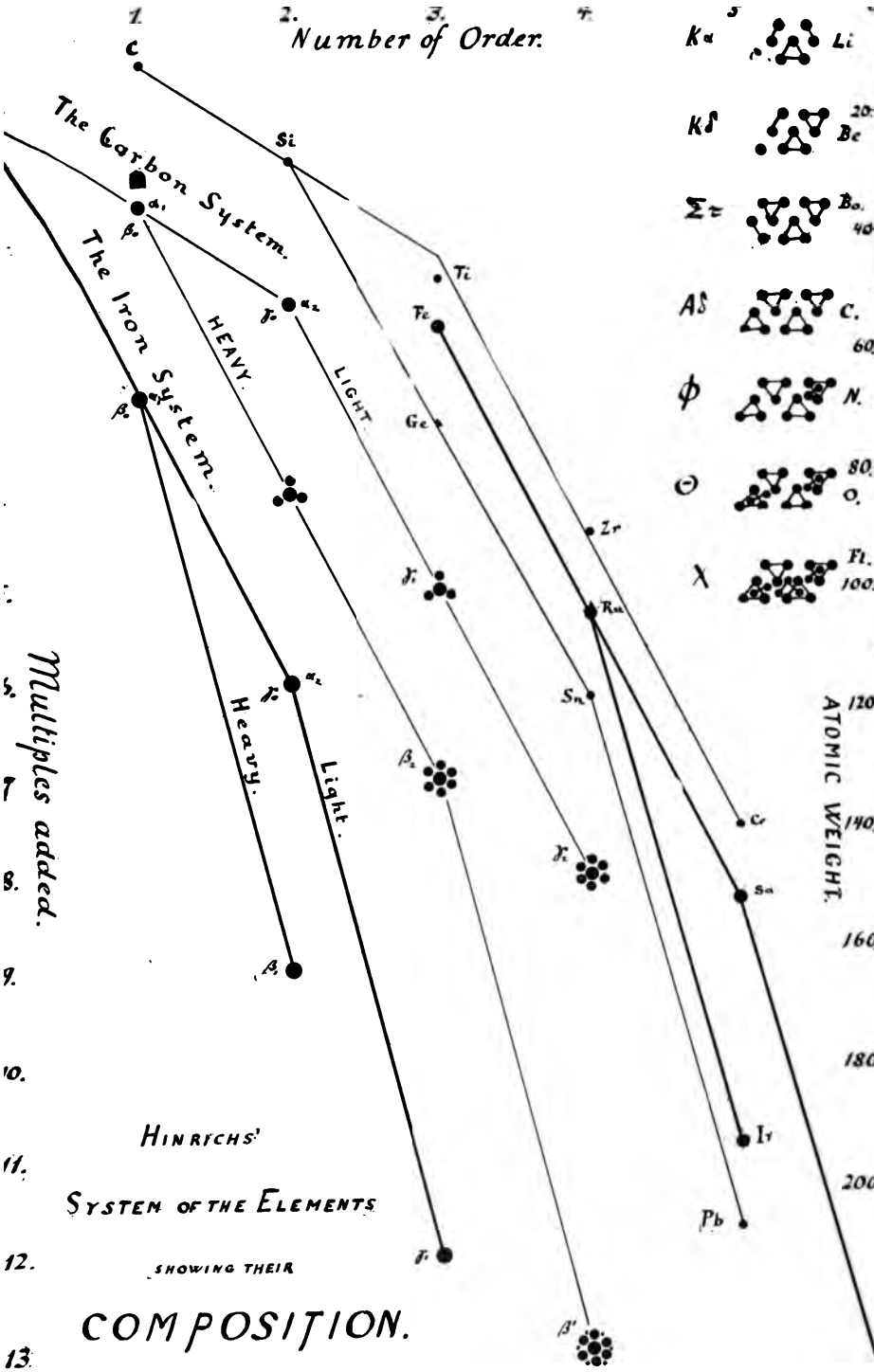
The following table gives the atomic weights* of these elements in their order of sequence.

Order:	0	1	2	3	4
Kaloids:	Li 7	Na 23	Ka 39	Rb 85.5	Cs 132
Chloroids:	Fl 19	Cl 35.5	Br 80	Io 127	?

Taking the number of order as abscissae, and the atomic weights as ordinates, we obtain the two lines marked by minute

*For elements for which I have not yet published my critical review, I take the nearest round number from Ostwald's Table: p. 126, l. c.

Volume III of my Elements is expected to contain full results of all my reductions of Atomic Weight Determinations. I shall be specially obliged for reprints of all papers on Atomic Weight Determinations.


Number of Order.
1.
2.
3.
4.
5
The Carbon System.
The Iron System.
HEAVY.
LIGHT
Heavy.
Light.
C
Si
Ti
Fe
Ge
Zr
Ru
Sn
Cr
Sn
Ir
Pb
Li
Be
Bo.
C.
N.
O.
Fl.
20
40
60
80
100
120
140
160
180
200
ATOMIC WEIGHT.
Multiples added.
HINRICHS'
SYSTEM OF THE ELEMENTS
SHOWING THEIR
COMPOSITION.

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TILDEN FOUNDATIONS

open circles in Figure 16, Plate IV. The symbols marked to the left or right will aid in finding the points referred to. The original drawing from which Plate IV is a photo-reduction was very carefully made on quite a large scale.

Joining these points by straight lines, we notice that the observations for each genus are represented by *two broken lines*, almost exactly parallel to the *broken limit line* marked A B C starting from the zero point A. We also notice that the limit line A B rises 16, while the limit line B C rises exactly three times as much for each number of order.

Hence the LIMIT of increase is for the Kaloids 1, 2, 5, 8 and for the Chloroids 1, 4, 7 times that limiting difference.

If we next consider the Calcoids and Cadmoids which already in my Programme of 1867 were shown to branch at Magnesia (See Fig. 15, and Plate VII), we have in the same manner as above

Order:	0	1	2	3	4
Calcoids:	.....	.....	Ca 40	Sr 88	Ba 137
Cadmoids:	Be 9	Mg 24	Zn 65.5	Cd 112	Hg 200

These genera are represented by the full black circles just below the Kaloids. The lines joining these points are almost exactly parallel to A B and B C; but there is added the line Cd—Hg almost parallel to C D, for which the increase is 6 times the original increment, or 6 Δ.

The central portion of this system starts with carbon. The elements are

Order:	0	1	2	3	4
Titanoids (?):	.....	.....	Ti 48	Zr 91	Ce 140
Adamantoids:	C 12	Si 28	Ge 73	Sn 118	Pb 207

The determinations for the Titanoids are rather uncertain, and the genus itself is not definitely located. All values are entered as larger black disks in Plate IV and joined by heavier lines. The front line, marking the Adamantoids, is in every way

well determined, however, and is seen to be nearly parallel to the limit line AB, BC, CD.

Nearly all other genera fall into lines parallel with these, starting parallel with the same limit AB and having therefore the differences Δ, 3Δ, 6Δ. The only notable exception thereto is the iron group, for which we have

Order:	0	1	2	3
Uranoids:	.....	.....	Sa 150	Ur 240
Sideroids:	Fe 56	Ru 104	Ir193	.....

These observations have been entered in Plate IV by the largest black disks and joined by the heaviest lines. The order number proper here is two lower than marked at the top of the diagram. The limiting differences in these genera are 3Δ and 6Δ since these lines are nearly parallel to the limiting lines BC and CD.

In Plate V (Fig. 17) the entire system is represented in outline. To the left, the systematic lines are drawn according to the limiting differences $\Delta=16$, $3\Delta=48$ and $6\Delta=96$. The corresponding points, representing elements are marked α, β, γ with indices of order. The second genus γ, is marked *light*, the first β, is marked *heavy*. This is descriptive of these elements, and will be understood as a necessary mechanical consequence of their structure given below.

Further to the right the systems proceeding from CARBON and from IRON are given in the true position as determined by the observed atomic weights. It will be noticed that the system lines are visibly parallel. The differences or increments must therefore correspond very nearly to the limiting values 16, 48 and 96, which are exactly as 1 : 3 : 6.

Accordingly, the chemical elements form two great, closely related, systems, the CARBON SYSTEM and the IRON SYSTEM. In addition we find the HYDROGEN SYSTEM consisting of hydrogen alone.

In each system we distinguish the following kinds of elements according to their structure shown in Plate V and implied in Plate IV:

MONADS, H, C, Fe, forming one compact prism of panatoms.

DYADS; α_1 *heavy* in which the monad has increased by one Δ in length, and α_2 *light* in which it has increased by 2Δ in length.

TRIADS, obtained from the diads by adding 3Δ twice in succession. They are *heavy* or *light* according as they are derived from the heavy β_0 or light γ_0 diads.

HEXADS result by the addition of 6Δ to the last of the heavy diads in the Carbon system.

In the Iron System we shall use the terms dyad and triad in a corresponding manner, though the latter is not quite exact, as readily will be seen.

Since we here purposely avoid entering upon theoretical questions, it will suffice to state that the method of increase exhibited in the Dyads has been set forth in the Programme of 1867, while the increase by Triads was first shown in my Principles of 1874 (p. 181, Fig. 41). These two principles cover the *outline* of the entire system which has its *body* filled out by the laws of atomicities as set forth in the Principles, p. 180. The following details will suffice in this preliminary publication.

DYADS, increasing from the monads in length merely, forming prismatic bodies, the limited increments will generally be the *true* one. That is, they will differ by 16 and 32 exactly, in most cases, from the monads. In the X and Φ there seems to be an exception requiring special examination.

TRIADS, increasing by 3Δ as in the ternaries with three atoms of oxygen (Carbonates), it is practically impossible to unite the Δ without loss, exactly as it is impossible to unite n.CH_4 without loss in hydrogen. This is plainly stated in the last two lines p. 181 of my principles, 1874. Accordingly, THE ACTUAL INCREASE

IN TRIADS MUST BE LESS THAN THE LIMITING $3\Delta = 48$; we may safely say, that if an atomic weight determination gives 48 exactly, it is too high. That such is the case can be readily seen both in Plate V and in Plate IV; for the lines drawn for the triads show a decided tendency to deviate towards the right downwards. In Plate IV this is particularly plain in the gradual approach towards the limiting line BC. The Kaloid-line is exactly parallel to AB; the next part converges visibly towards BC.

AS TO THE PRECISE AMOUNT OF THIS CHEMICAL TIE we can not give many exact data, because the exact determinations are still missing. The following examples will suffice.

In Kaloids we have Rb—Ka = 85, 5—39 = 46.5 and Cs—Rb = 132—85.5 = 46.5, so that the chemical tie is 1.5, or 0.5 for each $\Delta = 16$. This would mean one panatom missing—a monovalent tie, whereby the entire element atom is made a RIGID solid.

In the Adamantoids we have Ge—Si = 73—28 = 45, and Sn—Ge = 118—73 = 45, both exactly the same, or a tie of one unit for each Δ. The chemical combination is therefore twice as firm, as in the case of the Kaloids. The tie is divalent, measured in panatoms. We have also Pb—Sn = 207—118 = 89 which is twice 44.5, and shows a slightly stronger tie for the second series of Δ, as might have been expected.

In the Phosphoids the tie is 3 and 4 for 3Δ, and 4 in the Hexad. For the Sulphoids, the tie amounts to 1 and 2, while for the chloroids it is 3.5 and 1, quite irregular. I am strongly inclined to think that we do not yet know really pure iodine, and that all iodine so far has been contaminated with per-iodine, the still unknown hexad of that genus.

So long as no satisfactory determinations of the atomic weight have been made by the limit method, it is idle to enter upon more minute numerical details; THE GEOMETRICAL EVIDENCE

presented in my Plates IV and V IS THE MOST CONVINCING AND SATISFACTORY till such determinations shall have been made in strict accordance with my limit method.

Finally, the Monads C and Fe are modified each by removal (i. e. INCOMPLETE FORMATION) and ADDITION or surplus. This is illustrated in the upper right corner of Plate V, in accordance with the general law published in my Principles 1874, p. 180-181, arts. 501, 502.

The general formula of the atomic weight of the carbon monad of positive atomicity n as there given is

$$a = 20 - 2n$$

giving

Atomicity	1	2	3	4
a Calc	18	16	14	12
a Obs	Fl-1	O	N	C

In a like manner for structural atomicity we have

$$a = 5 - 2n$$

giving

Atomicity	–1	–2	–3
a Calc	7	9	11
a Obs	Li	Be	'Bo

The Monad of the IRON SYSTEM is (Programme 1867, p. 8, art. 33).

Cr.	Mn	Fe	Ni	Co
52?	55?	56	58?	59?

The MOLYDOIDS proper are Cr, Mo, Wo.

For common use my system may be printed in the following manner, omitting on principle, all the rare elements (earths) which are so imperfectly known. Their place would be immediately under the Calcoids.

HINRICHS' SYSTEM OF THE ELEMENTS.

GENERA.	SPECIES.				
Κα	Li	Na	Ka	Rb	Cs
Χα	.....	.....	Ca	Sr	Ba
Μλ	....	.....	Cr	Mo	Wo
Σδ	.....	.....	Fe	Ru	Ir
Πδ	.....	.....	Co	Pd	Pt
Κυ	.....	.....	Cu	Ag	Au
Κδ	Be	Mg	Zn	Cd	Hg
Στ	Bo	Al	Ga	In	Tl
Αδ	C	Si	Ge	Sn	Pb
Φ	N	P	As	Sb	Bi
Θ	O	S	Se	Te	?
Χ	Fl	Cl	Br	Io	?

In conclusion we may call attention to the following most general facts:

The MONADS known, forming the starting points of systems of chemical elements, are three

$$H=1,\ C=12,\ Fe=56.$$

There are indications of a fourth, in the neighborhood of 170; see Plate IV.

The only increment is $\Delta=16$, equal in weight to the element oxygen. It adds in full, as continuation to the monads, forming DYADS, corresponding to the binaries of ordinary chemistry. When clustering in threes and sixes around that prismatic dyad as axis, it of necessity represents "UNFINISHED OXYGEN" if we so may say, commonly lacking 0.5 (Kaloids Nos. 4, 5) or 1.0 (Adamantoids Nos. 3, 4) and even more (same, No. 5), in accordance with the chemical character of the element resulting.

In the organic world, the dominant constituent elements are C, H, O and N. We distinguish the Alcohol and Aromatic Series, or the Methyl and Phenyl Series.

In the inorganic world, the elements are referable to the systems of H (single), C and Fe. The Carbon system may be compared to the alcoholic, and the iron system to the aromatic series.

Oxygen is the dominant, active element in both organic and inorganic chemistry. In the mechanical constitution of the elements we recognize a group of exactly equal weight Δ, forming the dyads and, when unfinished, combining RIGIDLY with the diads to the triads, the heaviest of elements.

These triads will therefore be more readily decomposable than the dyads; the separated incomplete Δ would, however, instantly re-unite with any dyad present. For a more general consideration of this subject, see my Note,* Comptes Rendus, T. 115, p. 239, "On the Specific Heat of the Atoms and their Mechanical Composition."

Fig. 29.

a photogravure from
ose of tenth century.

and if it contained

the poison with the

IQUIDES as printed.

AND WHAT ABOUT THE POSSIBILITY OF MAKING GOLD? HAS ALCHEMY not been proved to be a chimera?—Let us see.

Cuproids:	Cu 63.5		Ag 108		Au 197
Differences:		44.5		89	
Adamantoids:	Ge 73?		Sn 118		Pb 207
Differences:		45?		89	

If these values were all firmly established, it might be possible to transfer the $6\Delta-7=89$ from lead to silver, and obtain Gold and Tin, provided that energy enough could be obtained to break off the Δ from the Pb, without affecting the silver; it might even be supposed possible to obtain gold by starting with copper and lead. Such reactions will, no doubt, first require energy of highest tension and in great amount; and secondly, such a pressure that Sn and Au can exist at a higher temperature than Ag and Pb. Of what material should the autoclave be made to obtain such transposition of the atoms? I do not know. Iron, Wolfram, or other members of the Iron System may be tried; for they are entirely different from the Carbon system and would probably not react under the same conditions. But to insist that the elements are specific, simple creations, that therefore it is ABSOLUTELY IMPOSSIBLE and CONTRARY TO REASON to make gold from baser metals, must hereafter be classed with the hasty generalizations of Empirics; for it has no scientific principle to rest upon.

It is a question of temperature and pressure that decides what a given organic mixture becomes in the common closed tube or in the autoclave.* It is very possible that it will be found equally a question of temperature and pressure only, whether the contents of an autoclave remains silver and lead or changes into tin and gold. Not only do the atomic weights aggregate

* In general, the reaction is determined by the formation of substances the tension of which is lowest, in the aggregate.—Thus, at 100° Water and Ethyl Chloride in closed glass tube yield Hydrogen Chloride and Alcohol; but when these two substances are heated to 150° under 40 atmospheres pressure, Water and Ethyl Chloride are obtained, as in the process of Gillard, Monnet and Bartier.

the same, but silver and gold are constitutionally related exactly as tin and lead, so far as our present experimental data permit us to see. The vapor tension of gold and tin appears to be less than that of lead and silver.

It is not for us to say what others may be able to accomplish, especially in the future. The entire history of science is marked by accounts of the doing of that which for ages had been declared impossible. When a student I was told that chemists cannot form organic compounds from inorganic materials; soon after, BERTHELOT published his grand "Chimie organique fondée sur la Synthése." Again, until recently, it was universally held that the diamond is a form of carbon that cannot be produced by the chemist from other forms of carbon; now, by skillful use of pressure and high temperature, MOISSAN has thrown this "Impossibility" into the same great Waste Basket into which progressive Science has thrown many other impossibilities, and into which it is sure to throw many more in the future.

NON POSSUMUS—very true; but those who succeed us would not be worthy of us, if they failed to do some things which are impossible to us.

IMPOSSIBLE is that alone which is contrary to reason and analogy. The chemical elements are clearly RIGID COMPOUNDS, corresponding to the NON-RIGID monaries, binaries and ternaries of ordinary chemistry. The constituent accretions of one may be transferred to another known to be able to unite with the same accretion. If this be agreed to, it is scientifically NOT IMPOSSIBLE from silver and lead to obtain gold. The autoclave is the powerful apparatus which has made modern organic chemistry what it is. In the hands of a Moissan of the twentieth century, the autoclave, charged with base metals, may yield pure gold.

The school of Baconian Empirics, spreading from the German Universities over the world, on the basis of what it considered absolute experimental demonstration of the highest scientific

order, has declared and loudly re-iterated for thirty years, that a common factor in the atomic weight of all chemical elements does not exist, and that the very idea thereof is a chimera. But we have dared to show, by their own experimental data, that they are in error.

Some of these leading German chemists are so constantly "chlorinating" that they seem to have lost the art of thinking; unhappily, they are writing all the time they do not work in the laboratory. Like "den Stundeslöse" of Holberg, they are altogether too busy with insignificant minutiæ.

For these reasons it is about time to recognize this state of affairs, and to give to their declarations of results the weight they are entitled to, but no more. The empiric popery in the science of to-day ought not to be left without the protest it deserves. We should return to the inductive methods of GALILEI, the true founder of Modern Science. Surely, that power, whatever it be, which has built up the wondrous diversity and transcendant beauty of mineral and organic nature from the few chemical elements, cannot have been unable to bring forth these few, closely allied elemental substances themselve from a single material, the PANTOGEN.

In the third Volume of the Elements of Atom-Mechanics we hope to show with much more detail and in a more thoroughly mathematical manner than we have sketched here or could do in our Programme of 1867, that the physical and chemical properties of the elements positively demonstrate this formation of the Chemical Elements—from the single primitive substance, the PANTOGEN, and that the UNITY OF MATTER is not a chimera, and not a dream, but a scientific reality.

SUPPLEMENTS.

I. My Natural Classification of the Elements.

As stated in a preceding page, I immediately arranged the radical system published in my Atomechanik of 1867 into a parallel line system suitable for printing. The black walnut blackboard, one meter square, mentioned below, has been in use nearly thirty years in my lectures; it is still so used, the symbols remaining unchanged. The large muslin charts—book form—have, however, been worn out.

On account of the historic importance of the subject I might here reprint in full the first publications made of this parallel line form, namely in the *Pharmacist* of Chicago, for July, 1869, and in the Proceedings of the American Association for the Advancement of Science at Salem, Mass., Vol. 18, pp. 112-124. We have already printed Part III of this paper, see pp. 65-69, supra; here we shall reprint Part I.

Since the paper in the Pharmacist is essentially the same as that read at Salem, only much more popular in form, I think it sufficient to reprint the latter.

"ON THE CLASSIFICATION AND THE ATOMIC WEIGHTS OF THE SO-CALLED CHEMICAL ELEMENTS, WITH REFERENCE TO STAS' DETERMINATIONS.

" [112] Like all other natural objects the chemical elements (so-called) can be classified into *natural* groups,—*Genera* made up of the individual elements as *Species* and *Varieties*. Such a classification was published in 1867 in my *Atomechanik* (§ 17, pp. 7, 8.)

"The symbol of the *species* is the characteristic letters of the [113] *Latin* name of the same, introduced by *Berzelius* in 1815; it has also a *numerical* value, representing the weight of the atoms.

"As symbol of the *genus* I introduced the characteristic letters of the *Greek* name of the same, and stated that this symbol represents an *equation*, the numerical value of which for the given variable would be the atomic weight of the species corresponding to that variable.

"The theoretical ground of this classification is exposed in *Atomechanik*. We shall here *exclusively* consider this question from a practical and empirical point of view, entirely independent of the pantogen-hypothesis. In this form it has now for two years been presented in my lectures.

I. CLASSIFICATION OF THE ELEMEMTS.

"This *empirical* classification (in its results *identical* with that of *Atomechanik*) is based mainly on the deportment of the elements toward *heat*. This physical agent being motion, *we accordingly classify the elements in regard to the mobility of their particles* (*the atoms*). We distinguish *six* degrees of *fusibility*, *three* degrees of *volatility*, and the *coloration of the flame* for the metals. We retain the general division of the elements in two *orders*, metals and metalloids, based upon the

presence or absence of metallic lustre. The above degrees of fusibility correspond very nearly to those of *von Kobell.*

"For farther explanation we may refer to the following *table*, merely adding, that the *name* of the genus was taken from the most common or more characteristic element. The Semi-barbarous name Sulphoid was chosen, because the more correct Thionoid is not so palpable to students.

[114] GENERAL TABLE OF THE GENERA OF THE ELEMENTS.

I. METALS, having metallic lustre.					
FUSIBILITY.	VOLATILE.	FLAME.	GENUS.		Representative Species.
			NAME.	SYMBOL.	
1	exceeding	color	*Kaloids*	*Ka*	*Ka*
2	very	no color	*Cadmoids*	*Kδ*	*Cd*
3	slightly	——	*Cuproids*	*Kυ*	*Cu*
4	not	color	*Calcoids*	*Xa*	*Ca*
5	not	no color	*Ferroids*	*Σι*	*Fe*
6 (infus)	not	——	*Titanoids*	*Tτ*	*Ti*
II. METALLOIDS, not having metallic lustre.					
Triatomic Elements like Phosphorus			*Phosphoids*	*Φ*	*P*
Di — " " Sulphur			*Sulphoids*	*θ*	*S*
Mon — " " Chlorine			*Chloroids*	*X*	*Cl*
Mon — " " Pantogen			*Pantoids*	*Υ*	*H*

"To these genera several others will have to be added; but not until the elements concerned are better known. Of such genera I mention here the Thalloids *θλ*, Molybdoids *Mλ*, Hydrargoids *Υγ* from *Atomechanik.* Beryllium is either the first species of the Ferroids or of the Cadmoids.

"The Ferroids are distinguished for their *varieties.* Thus the third species (Iron; Greek *Sideros*) is associated in nature and

in its properties with four varieties, which we term the *Sideroids* and give the symbol $\Sigma\delta$. They are Chromium, Manganese, Iron (*the* species), Nickel and Cobalt. They form a regular series, connecting Titanium of the Titanoids with Copper of the Cuproids (see Chart). The Rhodoids and Iridoids are not sufficiently known yet. Uranium is associated with Cobalt and the Sideroids, having exactly twice the atomic weight of Cobalt.

"The species in each genus are again arranged in the order of their volatility, *or* specific gravity, *or* atomic weight. By printing their symbols at distances from that of the genus, nearly proportional to the atomic weight, we obtain the following chart representing our classification of the elements. A few of the

HINRICHS' CLASSIFICATION OF THE ELEMENTS.

GENERA.			Species			
$x =$	1	2	3	4	5	
Y	*H*					
Kα	*Li*	*Na*	*Ka*	*Rb*		
Xα	—	—	*Ca*	*Sr*	*Bα*	
Kδ	—	*Mg*		*Zn*	*Cd*	*Pb*
Yγ	—	—		—	—	*Hg*
Kυ	—	—		*Cu*	*Ag*	*Au*
Σι		*Al*	*Co* *Ni* *Fe* *Mn* *Cr*	*Rh*	*Ir*	
Ττ	*C*	*Si*	*Ti*	*Pd* *Sn*	*Pt*	
⊕	*N*	*T*	*As*	*Sb*	*Bi*	
⊖	*O*	*S*	*Se*	*Te*	—	
X	*Fl*	*Cl*	*Br*	*Io*	—	
Y	*H*					

most important elements not embraced in the above ten genera have been added.*

"That this is a truly *natural classification* is proved by the fact that in this table the elements of like properties, or their compounds of like properties, form groups bounded by *simple lines*. Thus a line drawn through *C*, *As*, *Te*, separates the elements, having metallic lustre from those not having such lustre. The gaseous elements form a small group by themselves, the condensible chlorine forming the boundary. So also the boundary line of the *heavy metals* (specific gravity above five) is a simple line, running between *Kδ* and *Xa*, as far as the break in the vertical columns goes (to *Zn*), then down to *Ti* and through *Se* out between *Te* and *Io*. So also the boundary lines for other properties may be drawn.

"Of great practical importance are the lines expressing certain properties of definite compounds. Thus, the solubilities of Ternaries or Binaries in water. The reactions in the wet way (Fresenius). The blowpipe reactions, may be represented on such charts by means of a few simple lines. Such charts have been in use in my laboratory, and were exhibited to the Association—the symbols printed on muslin (size 8 × 6 decimeters) while the other details had been entered by hand. In the lecture room I also have been using a square blackboard of black walnut (one meter each way) with the symbols painted; a chalk line or figure then enters the property dwelt upon by the lecturer."

To this reprint we will add the following illustrations, referred to in the last two paragraphs, as *samples* of what was exhibited at Salem in the Meeting and what had been constantly used for two years previously before my classes in my lectures—and for a quarter of a century afterwards.

* The preceding chart is an exact photographic reproduction of the original print in the Proceedings; hence the misprint T for P could not be corrected.

The discovery of the Elements is two-fold; by ordinary chemical means and by the use of some new physical instrument.

Under the *first* we distinguish three periods: Antiquity, Alchemists, and Modern Chemical Analysis. The first two are specially marked on the chart; the last remains unmarked.

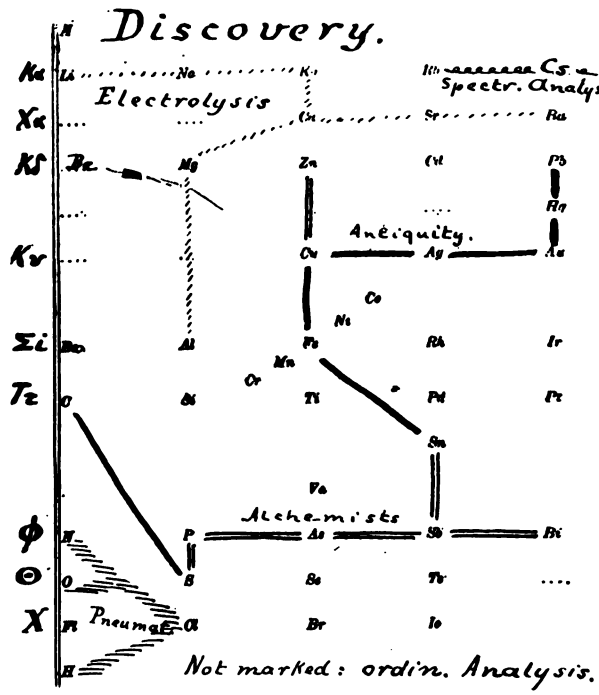


Fig. 19.

The *second* mode of discovery is also naturally divided into three distinct periods, characterized by the invention and introduction of special physical instruments, namely, the Pneumatic Trough (gases), Galvanic Battery (light metals) and the Spectroscope (flame coloration.)

The leading physical property of the elements, next to density, is their deportment toward heat. The fusing points are represented by lines of equal absolute temperatures.

It is seen that the iron group resists the most; from there both up and down the chart, the fusibility increases quite regu-

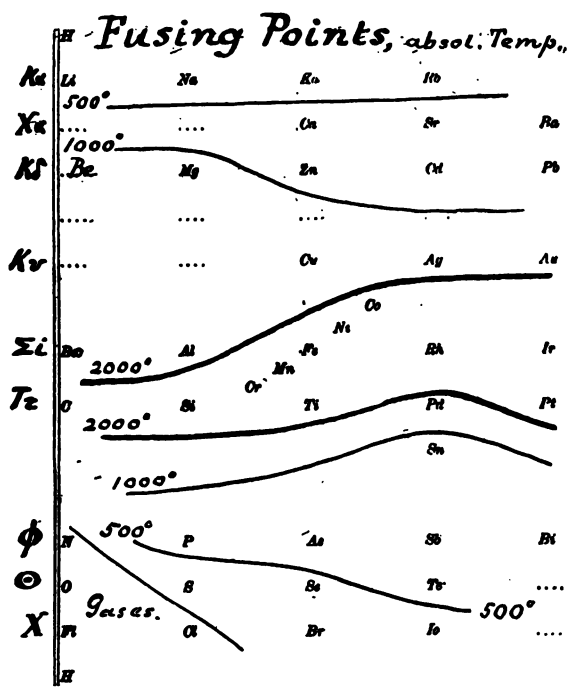


Fig 20.

larly as the volume diminishes. Sections laid through Na, Ka, etc., would give curves rising from below 500 degrees abs. to above 2000 in the iron group, and falling again toward the chloroids.

The elements in each genus are empirically arranged according to their specific gravity. The genera have, however, been arranged according to caloric and electrical deportment.

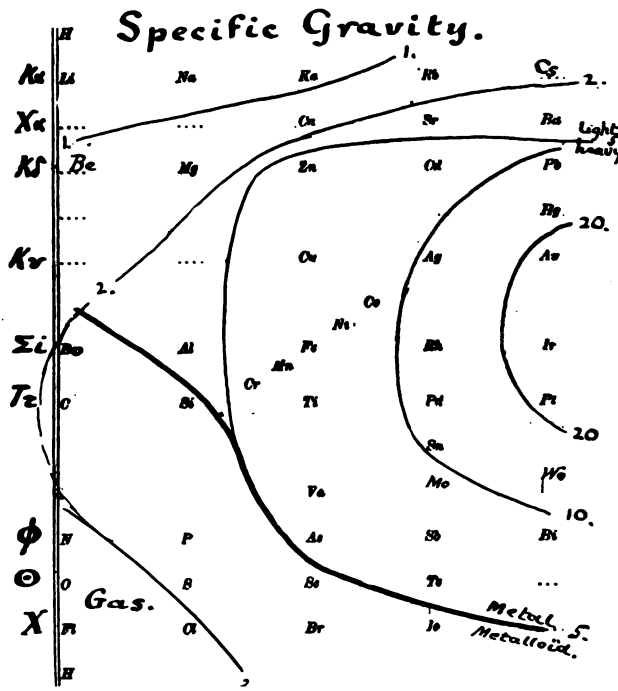


Fig. 21.

The chart shows that notwithstanding this fact, the genera are well grouped according to specific gravity also. The highest specific gravity (20) found from Au to Pt; the lines for 10, 5 and 1 are quite regular, as much so as if the genera had been especially arranged according to this property.

Dividing the specific gravity into the atomic weight gives the Atomic Volume. The chart here printed shows the lines of equal atomic volume for the values 5, 10, 15, 20, 25 and 50.

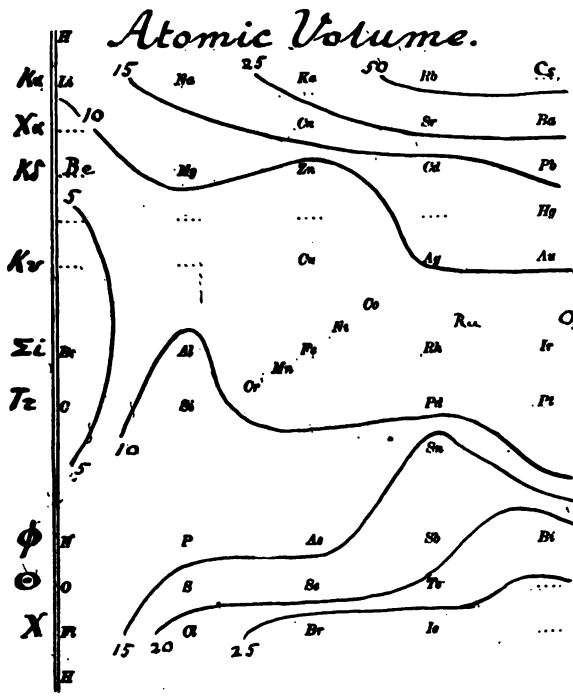


Fig. 22.

These lines are also quite regular. The lowest atomic volume we find in the iron group, from which it increases upward toward the Kaloids and downward toward the Chloroids. The atomic volume also increases more or less with the atomic weight in each genus.

The Blowpipe reactions also are exhibited by a very instructive chart. The residue *white* gives the two sub-fields, calling for cobalt solution or flame reaction.

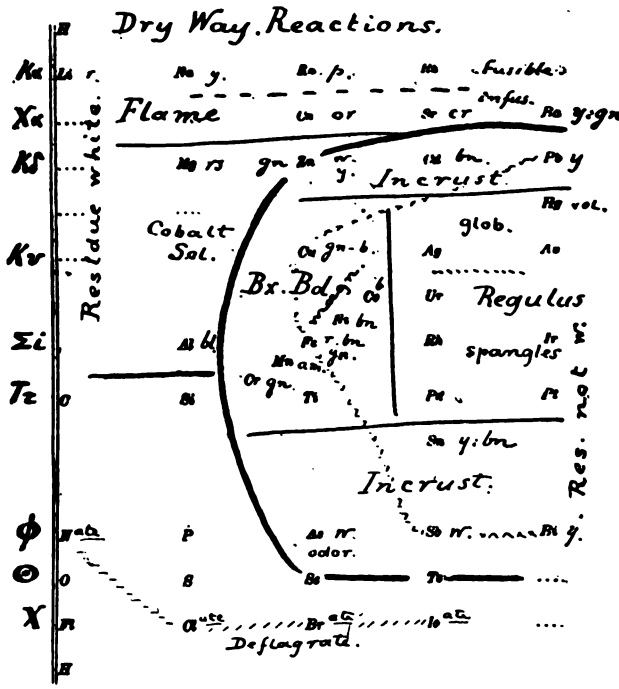


Fig. 23.

The residue *not white* is bounded by the heavy curved line. Incrustations are obtained only in the upper and lower parts thereof. The middle part gives in the right half only reguli, in the left half reguli and characteristic borax beads. The colors are entered near the symbol.

The Wet Way Reactions are equally well grouped on this system of the elements, as shown by the curves on this chart. Group I is precipitated as chloride, II as sulphate; III to VII as sulphide, namely in acid solution III, IV, V; in alkaline solution VI, VII. Group VIII is not precipitated by these general reagents.

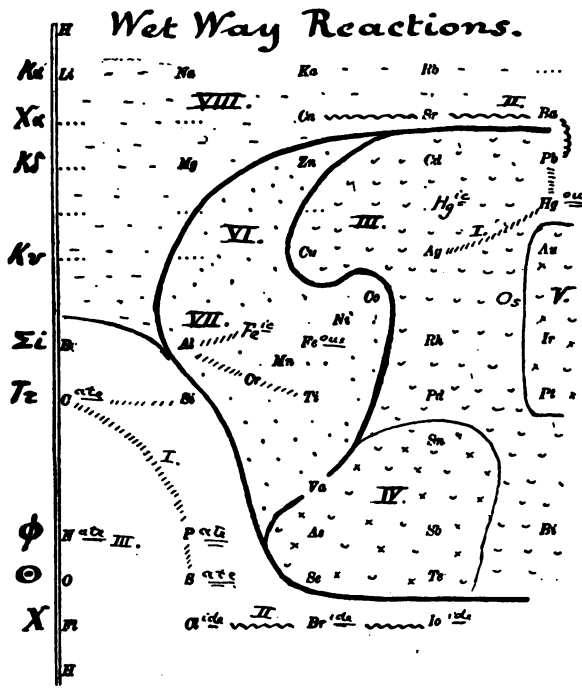


Fig. 24.

The sulphide precipitated in acid solution is insoluble in yellow Ammonium Sulphide III or soluble therein IV, V; if the last, V requires aqua regia for solution. The hydrates of VI are soluble, of VII resoluble in Ammonium Chloride.

The three principal groups of Acids are also indicated.

Exact, full size, photo-engraving of study and work blank used by myself. Also almost exact copy of Blackboard in Lecture Room.

Hinrichs' Classification of the Eleme

	H					
Ka	Li	Na		Ka		Rb
Xa	....	....		Ca		Sr
KS	....	Mg		Zn		Cd
	....	....		....		....
Kv	....	....		Cu		Ag
					Co	Ur
				Ni		
Σi	Be	Al		Fe		Rh
			Mn			
			Cr			
Tz	C	Si		Ti		Pd
						Sn
	Be			Va		
ϕ	N	P		As		Sb
⊖	O	S		Se		Te
X	Fl	Cl		Br		Io
	H					

Fig. 25.

These samples of illustrations show some of the charts which were exhibited before the Salem Meeting of the Americon Association in August, 1869. The charts actually exhibited were partly drawn in color, to show the color of the precipitates, incrustations, beads, etc.

The charts representing properties of the elements in numerical quantities allow the construction of common diagrams for both genera and order numbers, i. e., for the horizontal genus line as abscissa, or for the vertical lines of same order as abscissa. The quantities (specific gravity, and atomic volume, fusing point, etc.), thus become the ordinates.

But it must be apparent, that my diagram, representing the *surface* determined by the quantity in question, is for more general than either of the above. Hence, I prefer the representation of the surface. To obtain a description of the quantitative property, the form of this surface needs only to be described in words.

This process is complete, because it is mathematically exact. The same method is used in Meteorology and other branches of science where a function of *two* independent variables is to be represented.

Even to.day I see no reason to deviate from this method. A couple of symbols may now be placed differently—Pb in line with Sn, and these directly in line with C and Si. But on the whole, these changes, due to more exact knowledge of the relationship of a few elements, leave the main classification and the graphic representation of the properties of the elements by *Surfaces* entirely unchanged. This method gives the *whole truth*, and will remain the best that can be found.

II. THE PERIODIC LAW.

A couple of years after the publication of my *Programme der Atomechanik* the so-called Periodic Law was presented to

the chemical world by *Lothar Meyer* and by *Mendelejeff*. In a period of empiricism à l'outrance this "*law*" was promptly adopted and incorporated in text-books and presented in most of the chemical lecture halls throughout the world.

Being universally known, it is not necessary for me to give any details concerning the same. Our only object is to show that so far as it was new, it is not true, and so far as it is true, it was not new, but explicitly contained in my Programme of 1867.

One of these discoverors of the Periodic Law, LOTHAR MEYER was well acquainted with my Atomechanik, for he himself published a review thereof. The other discoverer, MENDELEJEFF, shows a little more originality in the handling of the subject, and may possibly have arrived at the result independently, though copies of my work were accessible to him. However, his publication was at least two years later than mine.

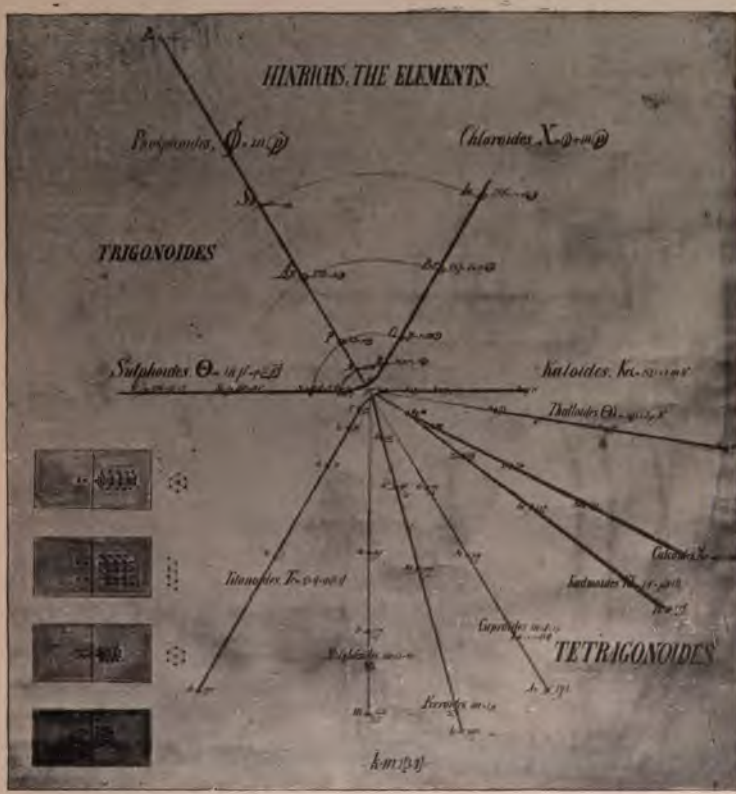
I am not willing to devote much space to this subject; it is not worth it, and the question is one that the *future* must and will pass upon. The following, it is hoped, will suffice for the present.

The elements are not mere periodic functions of their atomic weight, in any sense of the word. All *attempts to arrange the elements in regular, continued periods have absolutely failed.* Recurrances are real, but not at regular, equal intervals. The chemical and physical absurdities involved in this periodic law are, by common consent, overlooked to-day; but they are visible to all who will use their eyes — and some chemists will have their eyes open in tne future.

Furthermore, the very idea is mathematically absurd; a periodic function always implies more than *one* variable. If the atomic weight be the one compared, say to time, in astronomy—what is the other variable, corresponding to the orbit?

Mendelejeff shows that he has no conception of the subject

PLATE VII.



WALL CHART, 1867.

THE NEW YORK
PUBLIC LIBRARY
ASTOR LENOX
TILDEN FOUNDATIONS

(Note 11, p. 687-688). His entire book is almost as foggy as that of Lothar Meyer.*

But in my Programme (p. 7) the element atoms were represented as functions of weight and form, the form characterizing the genera of the elements. On page 9 all the well known elements were arranged in the system, the genera forming radii,

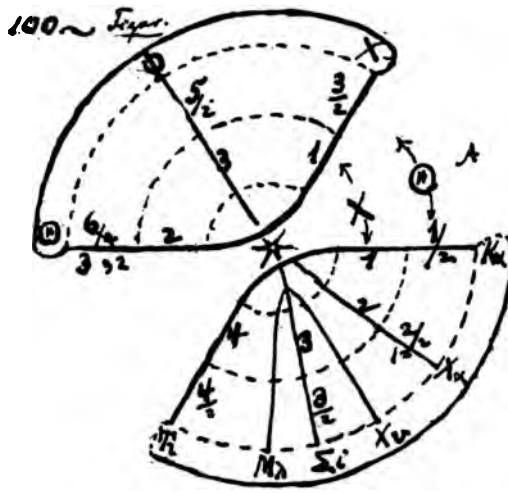


Fig. 26.

the species located at relatively large distances proportional to their atomic weights, and forming spirals.† Compare Fig. 15 printed p. 215; also the half-tone print (Plate VII) of a photo-

* RAU characterizes this book properly (III p. 265) in the following inimitable and almost untranslatable manner:

Indessen ist mir das Buch von *Wurtz* doch in vieler Hinsicht lieber, als das von *L. Meyer*; denn *Wurtz* schreibt mit einer gewissen graziösen Leichtigkeit, die das eigene Urtheil nicht erstickt, während *Meyer* in der Begründung unbegründeter Theorien eine breite Gelehrsamkeit entwickelt, die verblüffend wirkt; an ersterem wird sich Niemand den Verstand verrenken, bei letzterem kann es Einem passiren: es ist mit jener schweren, umständlichen, anscheinend aber bedächtig erwägenden, scheinbar umsichtigen und tiefsinnigen Gelehrsamkeit verfasst, die uns Deutsche in den schmeichelhaften, aber grundlosen Verdacht gebracht hat, ein Volk von lauter Denkern zu sein.

† My original conception was the arrangement on a right cone with π at the vertex. This brings the genera less far apart for the high atomic weight, but cannot be readily reproduced.

graph taken in 1867 from the wall chart which for twenty years was hanging near or over the experiment table in my lecture hall. In the balance of my "Programme" the physical and chemical properties of the elements are deduced from these *two* independents: weight and form of the atoms. Fig. 28 shows the chemical relations in the most conspicuous and compact manner (Atomechanik pp. 11-17).

The results were also empirically presented in charts, of which a few specimens have just been printed, pp. 232—237. The students even found blank forms of this system in the textbooks published by me; see my ELEMENTS OF CHEMISTRY, 1871, pp. 169-170. Extra printed blanks were also distributed from time to time.

Now these charts or diagrams present the properties *not* simply as function of *one* variable, atomic weight, for they could not possibly be function of one variable; it would be a mathematical and physical absurdity. These charts represent the properties of the elements as function of *both* the determining variables, atomic weight and form, the latter represented empirically by the name and place of the genus, but also by its own self in my Programme der Atomechanik of 1867.

Take my diagrams, cut them by vertical planes, put these in continuation according to the *order* of the genera — and you have all that the noted diagram of Lothar Meyer gives, who has constructed originally only one such (for atomic volume) and afterwards added the corresponding one for fusibility.—It takes a wonderful amount of imagination to see any regular periodicity in his diagram!

Now may I ask: since when is it proper in science to pass the complete — though compact — published exposition of new laws and discoveries by in silence, and to "sound fanfares of triumphal discovery," when some one who notoriously studied that work, takes in a most empirical manner a few shreds from

it, and before fully understanding it, coins a high sounding name for it, and publishes long articles and a big book about it, all as his own grand discovery?

The mere fact, that a book* like that of Lothar Meyer has experienced quite a run in Germany, the fifth edition of 626 pages having appeared in 1884, will no doubt in a near future be considered sufficient evidence of the present extreme empiricism of chemistry in that country; and the further fact, that in the multitude of empty words, rivalling in obscurity and indefiniteness with the worst specimens of the philosophic schools of antiquity and of the dark ages, it pretends to present a CHEMICAL MECHANICS when the author clearly has not even a rudimentary knowledge of MECHANICS himself, will soon be utilized as a warning against entering anew upon that empirical Baconian way. The final fact, that the vaunted discovery is simply an incompletely understood and miserably distorted conception of a work which the discoverer as critic condemned† in order to prevent its being compared to his spurious "law" completes the truly Baconian side of this subject.

So far as Mendelejeff if concerned, his publications on this subject in his GRUNDLAGEN DER CHEMIE, St. Petersburg, 1891, show the following special features:

1. Greater attention bestowed on the rarer elements, and
2. Bold, apparently successful predictions of new elements.

Concerning the first, it must be remembered, that only *time*

*Die modernen Theorien der Chemie.

† *Bischoff* in his *Stereochemie*, 1893, p. 15-16, quotes from Lothar Meyer's "Referat" in Zeitschr. für Chemiker, N. F. Bd. 6, 446, as follows:

"Lothar Meyer has found it impossible, considering the sketchy form of Hinrichs' presentation, to obtain a view of the degree of correspondence between the hypotheses of the author and the facts, and accentuates as especially suspicious that he uses partly dualistic formulæ (sic!), and that all considerations are based upon *Prout's Rule, which is well known to be erroneous!*"

Thus Lothar's object was accomplished. He knew the German chemical public. Lothar felt perfectly safe. His praises were sung in the German lecture halls. His colossal wall chart fitly corresponds to the colossal darkness prevailing, sufficient even to hide his dishonor.

will tell whether he was right in assigning these almost unknown elements the places he did. When we consider the numerous and most astounding blunders he has committed in placing the old, well known elements, such as Mn, Cr, Mo, Wo, all the cuproids and others, we may not be inclined to ascribe much weight to his location of the rare elements.

As to the prediction of *new* elements, Mendelejeff has reaped much renown from his eka-aluminum (Ga), eka-boron (Sc), and eka-silicon (Ge). Berthelot * has properly qualified this prediction (pp. 309-310, L'Alchimie). But besides, it should be distinctly understood that only the publication of actual predictions can be claimed for Mendelejeff; the PRINCIPLE on which the real predictions can be made, has been well stated in my Programme (art. 2, close) and the net-work necessary for the practice thereof was given p. 9 in the diagram Fig. 15 reprinted above (p. 215). But I preferred to indicate the method, without actually making specific prediction; the position in the nodes of the system or net-work will give all essential physical and chemical properties directly. In other words, the actual individual prediction is of no real value; † it is the net-work that determines all.

This is also made apparent by the fact that Mendelejeff and his admirers have only looked at one side of the medal; precisely as the ignorant weather prophets are in the habit of doing, who blow about the "hits" that necessarily must happen among any

* After taking many interesting and irresistible critical exceptions, he says, finally:

But this prevision, as has been said above, is not a consequence of the periodic series; it results purely and simply from the laws and analogies which have been known for many years, and which are independent of the new system.

† The real chemical work represented by Mendelejeff's prediction of Eka-Silicon is the recognition of C, Si, Sn, Pb as a true group. This is already contained in Meyers' first edition. 1864, p. 137, 1st column. My error of placing Pb was due to an under estimate of the importance of its organic compounds not fully known to me in 1867.

larger lot of hap-hazard predictions, but keep discreetly silent about their more numerous and glaring failures.

Thus, not a single element is known in the entire "row 9" of Mendelejeff; not one substance has ever been seen that could be twisted even by himself to fall into that line! We shall show that there never will be discovered an element belonging to that row. But this little fact of the failure to find any element and the significant demonstration of ours of its impossibility will have no effect on the empirics that worship the "periodic law." They will meet the observed fact and the laws of mechanics with some "neue Betrachtungen" and "interessante Ueberlegungen."

Having said this much, I suppose I am really bound to critically consider in detail a few points of this wonderful discovery of the Russian Chemist and the German Lothar.

Let us then copy Mendelejeff's own system from page 685 of his most barbarous GRUNDLAGEN DER CHEMIE; the greatest jumble of loose, endless notes and incoherent text that ever has been inflicted on chemists, and that has found a market solely because it comes from the "famous original discoverer of the *periodic law.*"

But there will be absolutely no use in our copying the symbols of the almost unknown elements that Mendelejeff has used to fill up the meshes of his net; we will, however, by the empiric be expected to give him credit for filling these spaces, so we will print the mark R wherever he claims to have located one of these practically unknown elements. His system then appears as printed here:

PERIODIC LAW OF MENDELEJEFF.

Group:	I.	II.	III.	IV.	V.	VI.	VII.	VIII.			
1	. H										
2	Li .	Be .	Bo .	C .	N .	O .	Fl .				
3	. Na	. Mg	. Al	. Si	. P	. S	. Cl				
4	Ka .	Ca .	Sc .	Ti .	Va .	Cr .	Mn .	Fe.	Ni.	Co.	Cu.
5	. (Cu)	. Zn	. Ga	. Ge	. As	. Se	. Br				
6	Rb .	Sr .	R .	R .	R .	Mo .	— .	Ru.	Rh.	Pd.	Ag.
7	. (Ag)	. Cd	. In	. Sn	. Sb	. Te	. Io				
8	Cs .	Ba .	R .	R .	R .	— .	— .	—	—	—	—
9	. —	. —	. —	. —	. —	. —	. —				
10	— .	— .	R .	— .	R .	Wo .	— .	Os.	Ir.	Pt.	Au.
11	. (Au)	. Hg	. Tl	. Pb	. Bi	. —	. —				
12	— .	— .	— .	R .	— .	Ur .	— .				

NOTE: The dash — indicates the place and character of an element predicted, but not yet discovered.

Now, beginning a brief critical examination of this system, we notice that the first three rows are not part thereof, having long been recognized in the relations here assigned them, with one generic exception. It is surely contrary to chemical and physical facts to set out the elements of row 3 as radically distinct from those of row 2. Li, Na, Ka and Be, Mg, Ca must be placed in the same line, or more strongly yet: Li, Na; Be, Mg; Bo, Al; C, Si; N, P; O, S; Fl, Cl, cannot possibly be considered as radically different, such as are Ka and Cu, or Ca and Zn, or Cr and Se, or Mn and Br. While then the enumeration in the first three rows is correct, having been established long ago, the *order* is entirely wrong, because

1ST. WE MUST PLACE ALL MEMBERS OF ROW 3 EXACTLY UNDER THE MEMBERS OF ROW 2.

This first fact already breaks up the entire system in which that ziz-zag constitutes a most essential part.

One of the greatest errors in the system of Mendelejeff is the strange position assigned to the iron group, practically outside of the system and beyond the chloroids, VII, which are supposed to gradually merge into the same. Group VIII is placed in rows 4, 6 and 10, and also as still unknown in row 8; that is, it is asserted to recur after two full "periods" namely at 4, 6, 8 and 10. The last member of VIII (our Cuproid) has been also inscribed in brackets under the first group in the next higher row thus forming a sort of connecting link in that direction—truly Darwinian. Now it is passing strange that at least three members are known in each one of the rows 4, 6 and 10, while not a solitary one is known in row 8. We shall learn that there is a most excellent reason for this, namely the fact that row 8 in the Iron group does not and cannot exist at all.

But every chemist must admit, that if Ni and Co belong to that Iron group row 4, Mn and Cr most assuredly ought to go there also. To compare Mn under Fl with Cl, and Cr under O

with S is supremely absurd,* and in absolute conflict with the best ascertained and most common chemical and physical facts. The oft used reference to "isomorphous" relations between Mn and Cl is so shadowy that, accepting it, we could place almost any element into a group with almost any other element.

I must declare it *impossible* to place Mn under Cl or Cr under S; the difference in atomic weight is 20, and it is impossible that the second dyad could differ by more than 16 from the first in the same genus.

As I have already stated in my Programme of 1867, Cr and Mn precede Fe as Ni and Co follow it in atomic weight; THESE FIVE ELEMENTS ARE UNDOUBTEDLY CHEMICALLY AND PHYSICALLY MEMBERS OF THE SAME SUB-GROUP and not related to either Cl or S.

I may add here, that Va and Ti also seem to belong to that group; the relations to P and Si are also through "isomorphism" mainly, while their physical and chemical differences are numerous and important, including the increase of 20 in the atomic weight. I did not intend to raise this point in this volume, because it is injudicious to consider this secondary matter at present.

But if Cr is taken out of group VI, Mo, Wo and Ur must come out also, and find some place in the great iron group. Accordingly we say

2ND. MN DOES NOT BELONG TO GROUP VII, AND CR, MO, WO, UR DO NOT BELONG TO GROUP VI; BUT ALL THESE ELEMENTS MUST BE CLASSIFIED WITH THE IRON GROUP UNDER VIII, WHICH HOWEVER, HAS NO REPRESENTATION IN ROW 8 AND CAN HAVE NONE THERE, and is not related to the chloroid elements.

Glancing down in VI, from O we now see nothing under it; the same in VII under Fl. We therefore conclude

* Tout ceci touche à la fantaisie. Berthelot, L'Alchimie, p. 310.

3RD. GROUPS VI AND VII HAVE NO EXISTENCE IN THE EVEN NUMBERED ROWS 4, 6, 8, 10 AND 12. They comprise therefore, only one genus each, the Sulphoids and Chloroids.

We find our Cuproids in two places, namely under the iron group VIII and under the Kaloids I; under the latter they are enclosed in brackets, evidently to indicate that they probably do not belong there. Surely, they cannot belong both to VIII and to I. It is strange indeed that Mendelejeff ever placed them under the iron group, VIII; neither physically, nor chemically, do they resemble members of the iron group. Nor are they Kaloids. The entire system of Mendelejeff being a hasty generalization, or possibly an inconsiderate empiric transcription from my Programme, my placing (in 1867) the cuproids on one side of the sideroids symmetric with the molybdoids on the other side, which was correct enough, seems to have been misunderstood by Mendelejeff. We now completely understand the position of the cuproids as triads of the *heavy* dyad Na, while Rb and Cs are the triads of the *light* dyad Ka. This fixes the position of the cuproids in relation to Iron exactly as I gave it in 1867. Accordingly,

4TH. THE CUPROIDS MUST BE REMOVED FROM THE VIII GROUP, AND LEFT RELATED TO I, as just explained.

One of the most remarkable predictions of Mendelejeff—about which he himself and his empiric admirers have maintained absolute silence—is the statement that there exists an element (see row 9) intermediate between Ag and Au*; also between Sn and Pb; also between Cd and Hg, as well as between Sb and Bi. We will not mention the fact that a corresponding "missing link" is predicted between In and Tl, for both of these are new members of the system. Beyond Te Mendelejeff makes us

* For the Cuproids in VIII this predicted metal falls in Row 8. It is only such a "missing link" that can be in two places at once — by not being at all.

expect two new elements; the same number must also exist beyond Io.

NOW, THIS IS ABSOLUTELY INCREDIBLE. Silver and Gold are so widely diffused, their properties are so marked and they are so easily distinguished from all other things on earth—in fact, gold and silver are undoubtedly the metals first known to man—that is truly incredible that an intermediate element should exist in nature and have escaped the searching hand of all mankind these thousands of years.

I do not like to follow Mendelejeff in the easy way of describing this * missing "*Asem*"; I am no friend of humbugs, and hate to make a show of profound learning and science while simply using the rudiments of arithmetic—say counting on the fingers of my hands. But— —

"Ahem"—the properties of this intermediate element between silver and gold which we may call "Asem" are fully determined by the Periodic Law in every detail with precision. It will show a brilliant metallic lustre, be more whitish than gold in color, extremely malleable so that it can be beaten into thin leaves, of which more than a hundred thousand will be required to make an inch; this still unknown metal will show a specific gravity between 14 and 15; in graphite crucibles it will melt at a fair white heat; it will not oxidize in air, give no incrustation on charcoal; etc., etc. It will dissolve difficultly in hot concentrated nitric acid, but may resist aqua regia. Acid solutions will be promptly precipitated by hydrogen sulphide gas, and the brownish precipitate will dissolve in yellow ammonium sulphide, etc., *ad nauseam.*

I repeat it, such talk is all humbug; the above *would* be the properties of such an intermediate metal, as every chemist will readily understand; *but the real question is*, DOES SUCH A METAL

* Alloys of gold and silver were called Asem by the Egyptians. Berthelot, Chimie des Anciens, Paris, 1889, p. 62. They first supposed it to be a metal.

EXIST IN NATURE? Surely, if it did, it would not have escaped nature's processes that have brought Silver and Gold so prominently to the attention of mankind even before the stone age, yea in the golden age of our race!

The fact that nothing of this kind has ever been found is sufficient proof that such an intermediate metal does not exist in nature, except in the imagination of our modern empirical chemists, some of whom have without labor or study become famous by "predicting" the existence of such elements as "asem." This is fame exactly of the same sort as falls to the lot of our noted storm predictors and publishers of weather almanacs, which sell by the tens of thousand in America, because Divine Providence has never allowed the fool killer to hurt anybody.

For tin and lead the same reasoning can be repeated, with much less force, we will admit, but yet without exposing ourselves to commit an error. But if that "missing link" between silver and gold is surely entirely imaginary and without shadow of substance, if we have neither found any such missing link between tin and lead, the entire row 9 of Mendelejeff is condemned as utterly without foundation in fact. Accordingly we have

5th. ROW 9 IS INDEED A CHIMERA, THE VAIN VAPORING OF AN EMPTY EMPIRIC BRAIN.

In row 10 the platinum metals are misplaced, Wo goes with them into the larger iron group; there remain only two rare metals R, supposed by Mendelejeff to be Ta and Yb. Since Mendelejeff knows no more about these elements than other chemists, who know next to nothing about them, and certainly have no positive knowledge of their atomic weight, it will be perfectly proper to declare that

6th. NO POTISIVE KNOWLEDGE IS AT HAND UPON WHICH THE EXISTENCE OF ANY MEMBER OF ROW 10 COULD BE PREDICATED; THAT ROW MUST, THEREFORE, BE ERASED ALSO.

While I am far from through with my critical consideration of

the famous periodic law* of Mendelejeff represented in his system of the elements as printed in his bulky and barbarous book which he declares to contain the Fundaments of Chemistry, I am tired and suppose the kind reader will allow me to take a rest. We shall therefore not consider the numerical fallacies of this system at present.

Let us now see what there is left of this famous system, after making the above corrections, and also omitting the almost unknown elements R.

	I	II	III	IV	V	VI	VII	VIII
1	H							
2	Li	Be	Bo	C	N	O	Fl	
3	Na	Mg	Al	Si	P	S	Cl	
4	Ka	Ca						Fe, Ni, Co.
5	Cu	Zn	Ga	Ge	As	Se	Br	
6	Rb	Sr						Ru, Rh, Pd.
7	Ag	Cd	In	Sn	Sb	Te	Io	
8	Cs	Ba						
11	Au	Hg	Tl	Pd	Bi	—	—	Ir, Os, Pt.
12								Ur.

Only that portion below line 3 can at all be credited to the famous periodic law. If we start with the form given by Lothar Meyer we shall obtain the same final results exactly.

Now Lothar was a student of my PROGRAMME DER ATOMECHANIK of 1867; for he published that noted "review" or "REFERAT" thereof quoted by Bischof. The classification of the elements which I presented in that book by diverging rays from the central pantogen, I immediately had arranged in parallel lines for more convenient printing and to obtain more compact diagrams, representing any given property of the elements as function of atomic weight and form. That transcription no one would dignify a discovery.

*That is something which in periods of scientific depression is accepted as law.

The classification presented by Meyer and Mendelejeff, in 1869, as the representation of the periodic law is practically identical with my own transcription of my radial diagram; for if a plane mirror AB be placed in vertical position just above the top of my chart, the mirror will reflect, as image of my own system, the exact arrangement of the periodic law. See Fig. 27. In this diagram I have placed the VIII corresponding to my own system instead of beyond the chloroids, VII, which position is absurd.

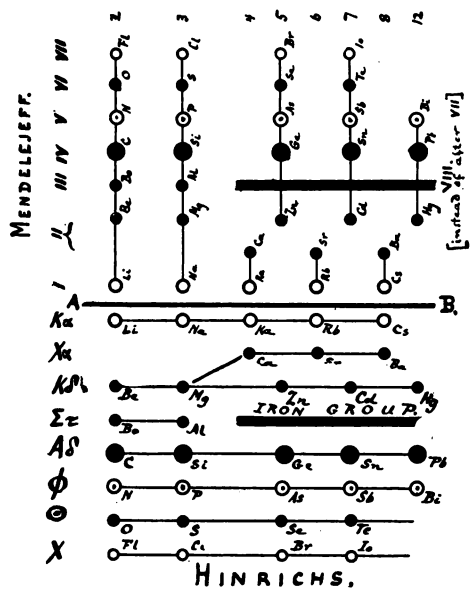


Fig. 27.

Nothing further need be said to demonstrate the real origin of that portion of the so-called periodic law which is true. That portion really discovered by Mendelejeff and Meyer we have shown to be false.

The atomic weights of Stas, and the periodic law together mark the chief results and the intellectual outcome of the empiric era of Inorganic Chemistry since 1860. It is doubtful if ever any other science of nature has reached so low a level as *scientific* Chemistry has done during the last third of a century. Great perfection in certain details, extreme expansion in patentable applications and in certain directions admitting "discovery" by wholesale in the formation of organic substitution compounds, are associated with an almost utter absence of sound scientific work and method, to such a degree, that positive error is heralded and proclaimed as highest truth and an absurdity, contrary to fact, admitted as a supreme new system, as a fundamental Law of Nature.

That in such a period, depraved chemists would be ready to commit scientific robbery is but natural. The highway robber strikes down his victim and then takes the purse and the watch. The would-be discoverer of chemical laws does essentially the same thing; but his club is professionally called the "Referat" in German.

When the robber thinks the referated victim is done with, perhaps scalped by the Indians, he publishes, as his own, so much of the book as his limited capacity can comprehend and puts it into the empiric form demanded by the fashion of the day under the high sounding title, The Periodic Law.

While nearly all prominent chemists during the past thirty years have fallen down and worshiped, it is cheering to know

that the greatest chemist of the age has flatly refused to bend his knee before Baal. Says BERTHELOT (L'Alchimie, p. 312):

"In fact, and to be sincere, we must say that beyond the old natural families of the elements, recognized a long time ago, the above (features of the periodic law) are hardly anything but artificial assemblages. Neither the system of periodic series, nor the system of multiples of hydrogen, has thus far furnished any certain and definite rule for the discovery of the new elements recently found, nor for the finding of those which we do not know yet. Furthermore, none of these systems has furnished a positive method, which will permit to foresee, even remotely, the synthetic formation of our elements; or which would point the way to experiments by which one might try to attain that end. Great illusions have arisen in this respect."

What Berthelot properly demands of a natural classification and a genetic system of the elements, I believe is sufficiently given in the third part of this treatise, which is but preliminary to the complete publication which I intend to give in the third volume of these ELEMENTS OF ATOM-MECHANICS.

From the popular errors of the day and the ephemeral coryphees of the present I turn to the great fountain head of modern inductive science, whose works have ever been a source of instruction, of inspiration and of comfort to me.

And now, at the close of the first one of the four volumes in which I hope to present the leading results of my forty years of labor, I come with reverence and humility to the great master, and ask permission to use the words Sagredo so justly pronounced at the close of Gjornata Terza, the grandest of them all — words of judgment which I have faithfully and earnestly striven to make applicable to this volume of mine on the Atoms and on the Elements:

Parmi veramente, che conceder si possa al nostro Accademico, che egli senza jattanza abbia nel principio di questo suo trattato potuto attribuirsi di arrecarci una nuova scienza intorno a un soggetto antichissimo.

GALILEO GALILEI.

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